FIC	2800
	2000

3

Questions about the scope or the results of the search? Contact the EIC searcher or contact:

Jeff Harrison, EIC 2800 Team Leader 571-272-2511, JEF 4B68

Voluntary Results Feedback Form								
> I am an examiner in Workgroup: Example: 2810								
> Relevant prior art found , search results used as follows:								
102 rejection								
☐ 103 rejection								
Cited as being of interest.								
Helped examiner better understand the invention.								
☐ Helped examiner better understand the state of the art in their technology.								
Types of relevant prior art found:								
☐ Foreign Patent(s)								
 Non-Patent Literature (journal articles, conference proceedings, new product announcements etc.) 								
> Relevant prior art not found:								
☐ Results verified the lack of relevant prior art (helped determine patentability).								
Results were not useful in determining patentability or understanding the invention.								
Comments:								

Drop off or send completed forms to STIC/EIC2300, CP4-9C13



Silicones

Matthew Butts, GE Global Research Center, Niskayuna, New York James Cella, GE Global Research Center, Niskayuna, New York Christina Darkangelo Wood, GE Global Research Center, Niskayuna

Christina Darkangelo Wood, GE Global Research Center, Niskayuna, New York

Gregory Gillette, GE Global Research Center, Niskayuna, New York

Rachid Kerboua, GE Global Research Center, Niskayuna, New York

John Leman, GE Global Research Center, Niskayuna, New York

Larry Lewis, GE Global Research Center, Niskayuna, New York

Suresh Rajaraman, GE Silicones, Waterford, New York

Slawomir Rubinsztajn, GE Global Research Center, Niskayuna, New York

Florian Schattenmann, GE Global Research Center, Niskayuna, New York

Judith Stein, GE Global Research Center, Niskayuna, New York

Jeffrey Wengrovius, GE Silicones, Waterford, New York

Denyce Wicht, GE Global Research Center, Niskayuna, New York

Encyclopedia of Polymer Science and Technology

Copyright © 2003 by John Wiley & Sons, Inc. All rights reserved.

DOI: 10.1002/0471440264.pst338

Article Online Posting Date: April 15, 2003

<Previous Next >

3. Polymerization

The manufacture of polydimethylsiloxane polymers is a multistep process. The hydrolysis of the chlorosilanes obtained from the direct process yields a mixture of cyclic and linear silanol-stopped oligomers, referred to as hydrolysate (eq. 11). In some cases, chloro-stopped polymers can also be obtained (102).

The ratio of cyclic to linear oligomers, as well as the chain length of the linear siloxanes, is controlled by the conditions of hydrolysis, such as the ratio of chlorosilane to water, temperature, contact time, and solvents (1). Commercially, hydrolysis of dichlorodimethylsilane is carried out by either a batch or continuous process (1, 2, 103, 104). In a typical industrial operation, dichlorodimethylsilane is mixed with 22 wt% azeotropic aqueous hydrochloric acid in a continuous reactor. The resulting mixture of hydrolysate and 32 wt% hydrochloric acid is separated by means of a decanter. After separation, the anhydrous hydrogen chloride is converted by reaction with methanol to methyl chloride, which is then reused in the direct process. The hydrolysate is washed to remove residual acid, then neutralized, dried, and filtered (105). The typical yield of cyclic oligomers is between 35 and 50%. The mixture of cyclic oligomers consists mainly of tetramer and pentamer. Only a small amount of cyclic trimer is formed.

The complete conversion of the dichlorodimethylsilane to only linear oligomers is also possible in a continuous hydrolysis operation (106). In this process, the cyclics are separated from linear oligomers by a stripping process and are mixed again with dichlorodimethylsilane. This mixture undergoes equilibration to chloro-terminated oligomers and is subsequently hydrolyzed. The silanol-stopped linear oligomers are directly used in the manufacture of silicone polymers.

Dichlorodimethylsilane can also be converted into siloxane silanol-stopped oligomers by a methanolysis process (eq. 12).

$$\begin{array}{c}
CH_3 \\
CI - Si - CI \\
CH_3
\end{array} \xrightarrow{+MeCl} \xrightarrow{+MeCl} \xrightarrow{+CH_3} \xrightarrow{CH_3} \xrightarrow{CH_3$$

In contrast to hydrolysis technology, the methanolysis process allows for the one-step synthesis of organosiloxane oligomers and methyl chloride without formation of hydrochloric acid (104, 107). The continuous methanolysis can also yield quantitatively linear silanol-stopped oligomers by recycle of the cyclic fraction into the hydrolysis loop.

If the linear fraction of siloxane oligomers is used directly in the manufacture of silicone polymers, extremely pure (greater than 99.99%) dichlorodimethylsilane is required. A high content of trichloromethylsilane can produce significant amounts of trifunctional units and considerably affect the

physical properties of the final products. If such high purity dichlorodimethylsilane is not utilized, an additional step, called cracking, must be included in the production scheme (108). In the cracking process, the hydrolyzate is depolymerized in the presence of strong base or acids to yield cyclic monomers, primarily octamethylcyclotetrasiloxane (D_4) and decamethylcyclopentasiloxane (D_5), which are distilled from the reaction mixture. The trifunctional byproducts remain in the pot and are periodically removed.

3.1. Polycondensation

Polymerization

The linear fraction of hydrolysate, dimethyloligosiloxane- α , α -diols having a viscosity of 10–100 mPa (=cP), is converted further to silicone fluids and high molecular weight gums by polycondensation of the silanol end groups (eq. 13). Polycondensation is an equilibrium process. In spite of the relatively high equilibrium constant for this reaction (K_{eq} (35°C = 860±90), water removal is required to obtain high molecular weight siloxane polymers (109).

Although the low molecular weight silanols such as trimethylsilanol and dimethylsilanediol undergo condensation thermally, the higher molecular weight oligomers are much more stable and their polycondensation must be catalyzed. Many catalytic systems capable of promoting polycondensation of siloxanediols have been described in patents and open literature (1, 110-117). These catalysts include strong acids such as HCl, HBr, H₂SO₄, HClO₄, and CF₃SO₃H; phosphonitrilic chlorides such as (Cl₃ PN(PCl₂N)_nPCl₃)⁺PCl₆⁻; oxygen-containing chlorophosphazenes such as Cl₃PN(PCl₂N)_nP(OH)Cl₂; strong bases such as KOH, NaOH, and (CH₃)₄NOH; as well as amines, amine salts of carboxylic acids, ion exchange resins, and clays activated with mineral acids. The most selective, efficient and extensively used in industry are phosphonitrilic chlorides (112-114) and oxygen-containing chlorophosphazenes (115-117).

The first mechanistic studies of silanol polycondensation on the monomer level were carried out in the 1950s (118-120). The proposed mechanism of the acid-catalyzed condensation involves the protonation of the silanol group and subsequent nucleophilic substitution at the silicone (eq. 14).

In the condensation catalyzed by a strong base the rate-determining step is the attack of silanolate anion on the silicon atom in the silanol end group (118, 119). Because of the high acidity of silanol (110), the alkali metal base (MtOH) is usually transformed into the silanolate anion (eq. 15).

Early studies of the condensation reaction on the monomer level did not give the full picture of this process and only in the 1980s the polycondensation of siloxanols was studied by using oligomeric model compounds (121, 122). These studies revealed that in the presence of strong protic acids three processes must be considered: linear condensation, cyclization, and disproportionation (eq. 16). The relative contributions from these processes strongly depend on the reaction conditions, such as type of solvent, substrate, water concentration, and acidity of catalyst (121-124). It was also discovered that in acid—base inert solvents, such as methylene chloride, another silanol group provides the basic assistance required for the condensation process. This phenomenon, called intra—inter catalysis, controls the linear-to-cyclic products ratio, which is constant at a wide range of substrate concentrations (121).

Linear condensation
$$HO\begin{pmatrix} CH_3 \\ Si-O \\ CH_3 \end{pmatrix}_{2n} + H_2O$$

$$\begin{pmatrix} CH_3 \\ Si-O \\ CH_3 \end{pmatrix}_n + H_2O$$

$$\begin{pmatrix} CH_3 \\ Si-O \\ CH_3 \end{pmatrix}_n + H_2O$$

$$\begin{pmatrix} CH_3 \\ Si-O \\ CH_3 \end{pmatrix}_n + H_2O$$

$$\begin{pmatrix} CH_3 \\ Si-O \\ CH_3 \end{pmatrix}_n + H_2O$$

$$\begin{pmatrix} CH_3 \\ CH_3 \\ CH_3 \end{pmatrix}_{n-1} + H_2O\begin{pmatrix} CH_3 \\ CH_3 \\ CH_3 \end{pmatrix}_{n+1}$$
(16)

The behavior of oligosiloxanediols in the presence of strong bases is different. The contribution to the overall process of the disproportionation reaction, involving a migration of the ultimate siloxane unit between siloxane molecules, is much greater and may even completely dominate the polycondensation reaction (125). The reactivity enhancement of the siloxane bond adjacent to the silanolate anion can be understood in terms of $n(0) \rightarrow \sigma^*(SiO)$ conjugation.

3.2. Ring-Opening Polymerization

Ring-opening polymerization of cyclic oligodiorganosiloxanes is an alternative to the polycondensation method of manufacturing siloxane polymers. Commercially, the polymerization of unstrained D_4 is the most important (1, 102, 110). In the presence of catalysts such as strong acids or bases, D_4 undergoes equilibrium polymerization, which results in a mixture of high molecular weight polymer and low molecular weight cyclic oligomers (eq. 17). The molecular weight of the polymer is easily controlled by the amount of chainstropper added and can be varied from very low molecular weight to very high molecular weight.

$$y = \frac{\text{CH}_{3}}{\text{CH}_{3}} + \text{H}_{3}\text{C} - \text{Si} - \text{O} - \text{Si} - \text{CH}_{3}}{\text{CH}_{3}} = \frac{\text{CH}_{3}}{\text{CH}_{3}} + \frac{\text{CH}_{3}}{\text{CH}_{3}} + \frac{\text{CH}_{3}}{\text{Si} - \text{O}} + \frac{\text{CH}_{3}}{\text{Si} - \text{O}} + \frac{\text{CH}_{3}}{\text{CH}_{3}} + \frac{\text{CH}_{3}}{\text{CH}_{3}$$

The position of the equilibrium depends on a number of factors, such as concentration of siloxane units and the nature of substituents on the silicon, but is independent of the starting ratio of linear to cyclics or the polymerization conditions (126, 127). For a bulk polymerization of dimethylsiloxane, the equilibrium concentration of cyclic oligomers is approximately 18 wt% (128). The equilibrium mixture of cyclosiloxanes is composed of a continuous population to at least D_{400} , but D_4 , D_5 , and D_6 make up over 95 wt% of the total cyclic fraction (129).

The ring-opening polymerization of D_4 is controlled by entropy, because thermodynamically all bonds in the monomer and polymer are approximately the same (1, 110, 130). The molar cyclization equilibrium constants of dimethylsiloxane rings have been predicted by the Jacobseon-Stockmayer theory (131). The ring-chain equilibrium for siloxane polymers has been studied in detail and is the subject of several reviews (127, 128, 132-135). The equilibrium constant for the formation of each cyclic is approximately equal to the equilibrium concentration of this cyclic, $K_n \sim [(SiR_2O)_n]_{eq}$. The total concentration of cyclic oligomers at equilibrium is thus independent of the initial monomer concentration. As a consequence, the amount of linear polymer decreases until the critical dilution point is reached, at which point only cyclic products are formed.

3.3. Anionic Polymerization of Cyclic Siloxanes

The anionic polymerization of cyclosiloxanes can be carried out in the presence of a wide variety of strong bases such as hydroxides, alcoholates, or silanolates of alkali metals (1, 102, 110). Commercially, the most important catalyst is potassium silanolate (98). The activity of the alkali metal hydroxides increases in the following sequence: LiOH < NaOH < KOH < CsOH, which is also the order in which the degree of ionization of their ion pair increases (136). Another important class of catalysts is tetraalkylammonium and tetraalkylphosphonium hydroxides, and silanolates (137-139). These catalysts undergo thermal degradation when the polymer is heated above the catalyst decomposition temperature (typically >150°C), producing volatile by-products and the neutral, thermally stable polymer. Recently, a new class of super-strong phosphazene bases such as $[(N(CH_3)_2)_3P = N -)_3P = N(t-C_4H_9)]$ have been reported (140-142). The phosphazene bases allow for the synthesis of high molecular weight polysiloxanes, using extremely low catalyst levels with short reaction times and over a wide range of temperatures.

Anionic polymerization is widely used in the silicone industry for the manufacture of silicone polymers. The anionic polymerization of cyclic siloxanes can be conducted in a single-batch reactor or in a continuously stirred reactor (143, 144). The viscosity of the polymer and type of end groups are easily controlled by the amount of added water or triorganosilyl chain-terminating groups.

The mechanism of anionic polymerization of cyclosiloxanes has been the subject of several studies (145, 146). The first kinetic analysis in this area was carried out in the early 1950s (147). In the general scheme of this process, the propagation/depropagation step involves the nucleophilic attack of the

silanolate anion on the silicon, which results in the cleavage of the siloxane bond and formation of the new silanolate active center (eq. 18).

The kinetics of this process is strongly affected by an association phenomenon. It has been known that the active center is the silanolate ion pair, which is in equilibrium with a dormant ion pair complex (148, 149). The polymerization of cyclosiloxanes in the presence of potassium silanolate shows the kinetic order 0.5 with respect to the initiator, which suggests the principal role of dimer complex (150).

The synthesis of new, high performance materials requires the synthesis of well-defined, narrow molecular weight distribution, cyclic-free, homo-, and copolymers. This can be accomplished by the kinetically controlled polymerization of the strained monomers, hexaalkylcyclotrisiloxanes. In the presence of the proper initiator and under the right reaction conditions, the polymerization of hexamethylcyclotrisiloxane (D₃) can proceed as a classical living polymerization. The most frequently used initiator, lithium silanolate, provides fast and quantitative initiation and a propagation that is free of depolymerization or chain-scrambling processes (151-153). However, the rate of D₃ polymerization in the presence of lithium silanolate is slow. To accelerate the polymerization process, a cation-interacting solvent such as tetrahydrofuran (THF) is commonly employed (154, 155). Nucleophilic additives such as hexamethylphosphoric triamide (HMPT) or dimethyl sulfoxide (DMSO), as well as chelating agents such as cryptates, can also be used (156-161). These additives interact strongly with the lithium cation and convert the intimate ion pair into a more reactive, separated one.

3.4. Cationic Polymerization of Cyclic Siloxanes

The cationic polymerization of cyclic siloxanes is often a preferred method for the synthesis of siloxane polymers. This process, which can be performed at relatively low temperature, can be applied to the synthesis of polysiloxanes having base-sensitive substituents such as Si—H, and the catalyst can be easily deactivated. The first high molecular weight siloxane polymer was prepared by the cationic ring-opening polymerization of D₄ in the presence of sulfuric acid (162). Since that time many catalytic systems have been reported in patents and open literature. These include strong protic acids such as CF₃SO₃H (triflic acid), HClO₄, H₂SO₄, aryl- and alkylsulfonic acids, heterogeneous catalysts such as ion-exchange resins, acid-treated graphite, and acid-treated clays, as well as some Lewis acids such as SnCl₄ (1, 110, 163-172). Polymerization in the presence of Lewis acids is a subject of controversy. Strong protic acids such as HSnCl₅, the product of the reaction of Lewis acid with water or other protic impurities, are proposed in most cases as the true catalyst (173). However, it has been reported that some nonprotic systems such as ethylboron sesquitriflate (174) and antimony chloride – acid chloride pairs (175) are able to initiate polymerization of cyclotrisiloxane. Also, electron-deficient organosilicone reagents such as trimethylsilyl triflate (176, 177) and Me₃SiH/(C₆H₅) 3C+B(C₆F₅)₄-(178) have been proven effective as initiators for cationic ring-opening polymerization of cyclosiloxanes.

Despite a long history of commercial application and in-depth studies (110, 163, 178-184), the mechanism of cationic polymerization of cyclic siloxanes is not as well understood as the anionic process. Several unusual kinetic results have been observed, such as the apparent negative order in the monomer concentration, negative activation energy, or a strong effect of water on the kinetics of polymerization (171, 182-185). The proposed complex mechanism of acid-catalyzed polymerization consists of four processes: initiation-ring opening, step growth by homo- and heterofunctional condensation, chain propagation by direct monomer addition, and end group interconversion. Hydrogen bond association plays a crucial role in this process (148, 185, 186). The cationic ring-opening polymerization initiated by the electrophilic trialkylsilyl species proceeds by the simpler addition mechanism, which involves a single "long-lived" oxonium ion end group (178).

3.5. Emulsion Polymerization

Even though siloxane bond formation is an equilibrium process, it is possible to form siloxane polymers by polycondensation or ring-opening polymerization in aqueous emulsions (187-189). D_4 can be converted into high molecular weight polymer by emulsion polymerization in the presence of dodecylbenzenesulfonic acid (DBSA), which acts as both emulsifying surfactant and catalyst (190). It is also possible to obtain high molecular weight polymers by polycondensation of α , α -dihydroxy-stopped oligosiloxanes in an aqueous emulsion employing DBSA (191) or benzyldimethyldodecylammonium hydroxide (BDDOH) (192) as the surface-active catalyst. The polycondensation involves the reaction of a complex of silanol and two molecules of DBSA with another silanol end group (193). The anionic emulsion polymerization of D_4 in the presence of BDDOH as a surface-active catalyst has been reported (192, 194) and a reaction scheme proposed, which involves a quaternary ammonium silanolate as an active species.

3.6. Radiation-Induced Polymerization

In 1956 it was discovered that D_3 can be polymerized in the solid state by Y-irradiation (195). Since that time a number of papers have reported radiation-induced polymerization of D_3 and D_4 in the solid state (196, 197). The first successful radiation-induced polymerization of cyclic siloxanes in the liquid state (198) and later work (199) showed that the polymerization of cyclic siloxanes induced by Y-irradiation has a cationic nature. The polymerization is initiated by a cleavage of Si — C bond and formation of silylenium cation.

The Y-irradiation-induced polymerization requires an extremely high purity reaction system. Trace amounts of water can terminate a cationic reaction and inhibit polymerization. Organic bases such as ammonia and trimethylamine also inhibit polymerization. The Y-irradiation-induced polymerization of rigorously dried D₄ exhibits a square-root dependence of the rate on the dose rate as predicted by the Hayashi-Williams equation for completely pure systems (200).

3.7. Plasma Polymerization

Plasma polymerization as a method for modifying surfaces of materials has been known for at least 25 years. The need for well-defined, thin polymer films for applications in optics, electronics, or biomedicine stimulated the development of plasma-induced polymerization but to date, relatively few large-scale applications exist. However, in recent years increased awareness of energy consumption and hazardous waste disposal concerns have stimulated the interest in this technique as a method for manufacturing or depositing polymers on various substrates (201). The special interest that has developed in organosilicon monomers may be because many of these monomers are generally volatile, nontoxic, nonflammable, and relatively inexpensive. Also, plasma-polymerized organosilicone films have a natural chemical affinity for adhesion to single-crystal silicon, and the properties of these films can be varied widely by the choice of monomer and polymerization parameters (202). The mechanism of plasma polymerization is still not well understood as of this writing and differs substantially from the conventional ring-opening polymerization of cyclic monomers. The dissociation and ionization of organosilicone monomers by low energy electron impact is the dominant source of radical fragments and a variety of ion-molecules and ion-radicals. In the case of hexamethyldisiloxane, extension of the monomer molecule by one dimethylsiloxane unit and elimination of the trimethylsilylium ion, (CH₃)₃Si⁺, was proposed as a crucial step in the polymer film formation. The building of Si — C — Si links also plays an important role in the polymerization. Cyclic monomers such as D₄ polymerize via the formation of a network of siloxane chains and rings. The resulting films are usually hard and scratch-resistant but often show considerable stress (203). Such films can be used as corrosion-resistant coatings on metals or as membranes in gas sensor devices (204, 205). The plasma polymerization of tetramethyldisiloxane was recently employed

3.7.1. Silicone Network Formation

Silicone rubber has a three-dimensional network structure consisting of cross-linked polydiorganosiloxane chains. Three reaction types are generally employed for the formation of silicone networks (207): peroxide-induced free-radical processes, hydrosilylation addition reactions, and condensation reactions. Silicones have also been cross-linked using radiation to produce free radicals or to induce photoinitiated reactions.

3.8. Peroxide Cure

The use of peroxide catalysts at elevated temperatures is one of the most common methods for the preparation of silicone networks (208). Typical peroxides include acyl derivatives such as dibenzoyl (209), bis-p-chlorobenzoyl, and bis-2,4-dichlorobenzoylperoxides; arylalkyl derivatives such as dicumyl peroxide; and dialkyl derivatives such as di-t-butyl peroxide and 2,5-dimethyl-2,5-di-t-butylperoxyhexane. The amount and type of peroxide used determine the cure temperature of the composition as well as its ultimate properties. Diaroyl peroxides can be used with either PDMS or with vinylmethylpolysiloxanes. Bis-2,4-dichlorobenzoyl peroxide has the highest rate of decomposition and the lowest decomposition temperature. Cross-linking by peroxides is initiated by the generation of free radicals via homolytic cleavage of the peroxide at elevated temperatures. The peroxy radicals can abstract hydrogen atoms from methyl groups, forming ethylenic linkages between siloxane chains (210). Model studies have confirmed the formation of SiCH₂CH₂Si as the predominant cross-linking reaction (211).

$$ArOOAr \longrightarrow 2 ArO \cdot$$

$$ArO \cdot + CH_3SiR_3 \longrightarrow ArO \cdot + CH_2SiR_3$$

$$2 \cdot CH_2SiR_3 \longrightarrow R_3SiCH_2CH_2SiR_3$$

$$(19)$$

The cross-linking of vinyl containing polydimethylpolysiloxanes can be achieved using alkylaryl or dialkyl peroxides (1, 212). A radical can be formed at either the methyl or vinyl site; it is generally agreed that the reaction through the vinyl group is energetically favored. Several mechanisms have been proposed to explain the reaction. One suggestion is that the radical is first formed on a methyl group that can then attack either a methyl group or a vinyl group (213). Another proposal is that the cross-link occurs primarily through the vinyl group (214). The first step is addition of the peroxy radical to the vinyl moiety (215). The resultant radical can then attack either another vinyl group or a methyl group. Termination can occur by coupling or by hydrogen abstraction from adjacent peroxide molecules. Rheometric studies indicate that methylvinylsilicone resins do undergo cross-linking via the methyl groups but at a slower rate than through the vinyl groups (216).

3.9. Hydrosilylation

Hydrosilylation, the reaction between a silicone hydride group and an olefin to form an alkylenic linkage, is extremely important for the formation of silicone networks (77, 83, 217-219). Cross-linking and network formation occur by reaction of multifunctional silicon hydride groups with multifunctional silicone olefinic groups. Typically, vinyl groups attached to silicon are employed; however, there are reports of network formation by reaction of multifunctional silicone hydride polymers with hexenyl-terminated siloxanes (220). No by-products aside from Pt residue are produced by this type of curing and no shrinkage is observed. Addition of the hydride to the olefin may be either Markovnikoff or anti-Markovnikoff, depending upon the choice of the silicone—

olefm group and catalyst. With silicon-bound vinyl groups, the reaction produces 95% of the β -addition product.

Hydrosilylation is generally catalyzed by Group 8–10 (VIII) metal complexes or supported metal catalysts. Platinum complexes are the most widely used, although rhodium(I) complexes have also been reported (83). Typical industrial catalysts include soluble platinum species such as the platinum—divinyltetramethyldisiloxane complex (Karstedt's catalyst) (221). These catalysts exhibit high turnover rates and are useful in concentrations as low as 1–2 ppm.

Side reactions or postcuring reactions are possible in the formation of silicone networks. In most cases, the silicon-bound hydride is in stoichiometric excess to enhance reaction rates. Disproportionation reactions involving terminal hydride groups have been reported (222). A major side reaction consumes Si — H to give redistributed siloxane in the resulting polymers and gaseous silane as a by-product.

Excess silicon hydride may undergo hydrolysis. The silanol thus formed can then condense with another hydride, resulting in networks with a higher cross-link density (223-225). Isomerization of a terminal olefin to a less reactive internal olefin has been noted (222). Vinylsilane/hydride interchange reactions have been observed particularly when less active catalysts are employed (217).

$$R_3SiH + R'_3SiCH = CH_2 = R'_3SiH + R_3SiCH = CH_2$$
 (21)

Several mechanisms have been proposed for the platinum-catalyzed homogeneous hydrosilylation reaction. The most commonly invoked mechanism, proposed by Chalk and Harrod in 1965, consists of elementary steps similar to homogeneous hydrogenation, oxidative addition, migratory insertion, and reductive elimination (226). However, this mechanism fails to describe the induction period or the presence of colloidal species at the end of the reaction. Lewis proposed an alternative mechanism based on the intermediacy of colloids that were detected by transmission electron microscopy after evaporation of catalytically active solutions (227, 228).

More recently, extended X-ray absorption fine structure (EXAFS) has been used to identify the actual catalytic species in both model systems and networks (229). At the completion of the hydrosilylation reaction, the state of the platinum species is dependent upon the reaction conditions. With a stoichiometric excess of olefin, a mononuclear platinum species containing six platinum—carbon bonds, such as platinum coordinated to three olefin groups, is obtained. However, in the presence of high silicon hydride concentrations or in reactions employing poorly coordinating olefins such as hexenes, the platinum product is multinuclear and contains platinum—silicon bonds. Upon addition of the deficient reagent (olefin or silicon hydride), the platinum products can interconvert to the catalytically active form. Colloids have been found in a postmortem analysis of hydrosilylation reactions upon evaporation or destabilization of the reactant solutions. EXAFS analysis of solutions frozen during model reactions of cross-linking systems (functional siloxane monomers) showed that regardless of reactant stoichiometry, the platinum intermediates during the catalytic portion of the reaction were mononuclear and contained both platinum—silicon and platinum—carbon bonds. A mechanism was therefore proposed that incorporates the Chalk—Harrod postulate with the addition of exchange and hydrosilylation of the ligands on the platinum during the induction period, and a pathway to colloid formation at the end of the reaction. Ab initio calculations reported on the platinum—catalyzed hydrosilylation of ethylene support the Chalk—Harrod mechanistic steps of oxidative addition, migratory insertion, and reductive elimination during the catalytic cycle (230).

Catalyst inhibitors are often included in formulations to increase the pot life of these systems. An ideal silicone addition cure composition would combine instant cure at elevated temperature with infinite pot life at ambient conditions. Unfortunately, real systems always deviate from this ideal situation. One mechanism of inhibition consists of equilibrium between the inhibitor (I) and catalyst ligands (L) (231).

$$PtL_n + x I = PtL_{n-x}I_x + x L_n$$
(22)

Hydrosilylation with inhibited complexes is generally less rapid than with platinum(0) olefin compounds. Complexing ligands such as phosphines and amines are excellent inhibitors but often form complexes so stable that they act as poisons and prevent cure even at elevated temperatures. Unsaturated organic compounds such as acetylenic alcohols, acetylene dicarboxylates, maleates, fumarates, and energies are preferred inhibitors (231-242). Steffanut and coworkers (243) have reported the use of platinum(0) complexes with electron-deficient olefinic ligands as hydrosilylation catalysts. Some of these complexes are self-inhibiting. Platinum—fumarate or maleate complexes formed from the reaction of platinum(0) compounds with dimethyl fumarate or dimethyl maleate must undergo reduction of the fumarate or maleate ligand with silicon hydride, prior to becoming active hydrosilylation catalysts (244). An alternative inhibition strategy is to encapsulate the platinum catalysts with cyclodextrin, thermoplastics, or silicones (245-247).

3.10. Condensation Cure

The condensation of silanol groups to form siloxanes is an extremely important industrial reaction and may be represented in its simplest form as follows:

$$R_3SiOH + R_3'SiOH \rightarrow R_3SiOSiR_3' + H_2O$$
 (23)

Unfortunately, because self-condensation of silanols on the same silicone can occur readily, the controlled reaction of disilanol or trisilanol compounds with telechelic silanol polymers to form a three-dimensional network is not feasible. Instead, networks are derived from reactions of telechelic polymers with cross-linkers containing reactive groups such as alkoxysilanes, acyloxysilanes, silicon hydrides, or ketoximinosilanes, as in the reactions 24, 25, 26, 27 (207). The choice of the cross-linking agent depends on the specific product characteristics desired.

$$R_3SiOH + R_3'Si(OCH_3) \rightarrow R_3SiOSiR_3' + CH_3OH$$
 (24)

$$R_3SiOH + R_3'Si(OOCCH_3) \rightarrow R_3SiOSiR_3' + CH_3COOH$$
 (25)

$$R_3SiOH + R_3'SiH \rightarrow R_3SiOSiR_3' + H_2$$
 (26)

$$R_{3}SiOH + R'_{3}Si(ON = C - CH_{2}CH_{3}) \longrightarrow R_{3}SiOSiR'_{3} + HO = N - C - CH_{2}CH_{3}$$

$$CH_{3}$$

$$CH_{3}$$

$$(27)$$

Condensation catalysts include acids and bases, as well as organic complexes of metals. Both tin(II) and tin(IV) complexes with oxygen-donor ligands are extremely useful. It has been suggested that the tin(IV) catalyst is converted to its active form by partial hydrolysis followed by reaction with the hydrolyzable silane to yield a tin-silanolate species (eqs. 28 and 29) (248, 249).

$$R_2Sn(OCOR')_2 + H_2O \rightarrow R_2Sn(OCOR')OH + R'COOH$$
(28)

$$R_2Sn(OCOR')OH + Si(OR')_4 \rightarrow R_2Sn(OCOR')(OSiR')_3 + R'OH$$
(29)

The organotin silanolate reacts with the PDMS diol by either attack on the SiOC bond or by silanolysis of the SnOC bond (248, 249). Other metal catalysts include chelated salts of titanium and tetraalkoxytitanates, which have also been shown to form silanolate species similar to those postulated for tin catalysts (250, 251). Formation of a cross-linked matrix involves a combination of the three steps in equations 30, 31, 32.

$$R_3'Si(OR) + H_2O \rightarrow R_3'SiOH + ROH$$
 (30)

$$R_3SiOH + R_3'SiOH \rightarrow R_3SiOSiR_3' + H_2O$$
(31)

$$R_3'Si(OR) + R_3'SiOH \rightarrow R_3'SiOSiR_3' + ROH$$
 (32)

The role of water in condensation cross-linking is dependent upon whether the material is a one- or two-component curing system (252). One-component systems do not cure until they are exposed to water. Two-component systems usually contain water in one of the components and begin to cure as soon as the components are mixed. Other work suggests that tin(II) catalysts can function in the absence of water (253). Studies of the relative rates of hydrolysis and condensation of multifunctional silanes, $R_x Si(OR)_{4-x}$, in the presence of acidic or basic catalysis have shown that the first $Si \longrightarrow OR$ group hydrolyzes much more rapidly than subsequent groups (254). Silanol-silanol condensation is much slower than silanol-alkoxysilane condensation, even if the alkoxysilane is monofunctional, thus suggesting that in the presence of a cross-linker, chain extension will not occur to a significant extent (255-258).

Condensation cure can also be carried out in emulsions (259-271). In this case, the cross-linker and PDMS are emulsified using anionic, cationic, or nonionic surfactants in water, and a condensation catalyst such as dibutyltin dilaurate is added. The formulation can also be cured without a tin-catalyst if self-catalytic hydrolyzable silanes are included (265). The polymer can then undergo cross-linking, forming a continuous film when the water is evaporated.

3.11. High Energy Radiation Cure

Silicones can be vulcanized by high energy radiation examples of which include Y-irradiation, X-ray, and electron beam. High energy radiation interacts with shell electrons of atoms of the silicone materials and induces ionization. The generated radical cations and free radicals initiate chemical reactions that lead to cross-linking (272). The properties of silicones cross-linked by high energy irradiation are indistinguishable from those vulcanized with peroxides (273). But

silicone rubber cross-linked by Y-irradiation does, however, have two advantages: better resistance to aging in humid environments and greater hydrolytic stability at elevated temperatures because the compositions are catalyst-free (274). Radiation cure of methylvinyl silicone rubber is a random cross-linking process with no differentiation between methyl and vinyl groups (275). Substitution of phenyl for methyl groups on the siloxane chain increases the radiation resistance. Silicone hydride groups are highly sensitive to radiation (276).

3.12. Photoinitated Radiation Cure

Attachment of reactive functional groups such as mercaptans, acrylates, and oxiranes to a polysiloxane backbone can be used to render a silicone susceptible to curing by lower energy electromagnetic radiation such as ultraviolet (UV) or low energy electron beam (EB) (277). Thiols can be added across an olefin using an aromatic ketone as the photoinitiator (EB) (278, 279). Unfortunately, the odor associated with thiols has limited the commercial acceptance of this technology. Two systems, which are widely used in the industry for silicone release and protective coatings, are silicones containing pendent acrylate groups (free-radical cure mechanism) and oxirane or vinyl ether functional siloxanes (acid-catalyzed). The acrylate functional polysiloxanes are prepared by allowing epoxy-functional siloxanes to react with acrylic acid or from the esterification of siloxane containing alcohol groups with acrylic acid (280-283). Cross-linking occurs upon the generation of free radicals by EB irradiation of the silicone matrix or by UV-initiated decomposition of benzophenone-based photoinitiators. The most important limitation of this process is sensitivity to oxygen. The typical industrial coating line requires oxygen levels below 50 ppm.

Silicones functionalized with oxiranes or vinyl ether groups can be cured by UV irradiation in the presence of diaryliodonium or sulfonium salts containing triflate, PF₆, or SbF₆ counterions (284-290). Decomposition of the onium salt under UV irradiation leads to the formation of strong acid that initiates very rapid polymerization of oxiranes or vinyl ether groups (291-293). Recently, a new class of onium salts prepared with the tetrakis(pentafluorophenyl)borate (TPFB) anion has been introduced as a UV photoinitiator (294-296). The presence of the large, weakly nucleophilic TPFB anion improves the solubility of the iodonium salts in the siloxane matrix and increases the reactivity of the formed acid (297, 298). The cationic polymerization of oxiranes and vinyl ethers is not sensitive to the presence of oxygen and can be carried out under ambient conditions. Cycloaliphatic epoxies are highly reactive in the ring-opening polymerization reaction initiated by strong acids and so the typical commercial system is based on polysiloxanes with pendent cyclohexeneoxide moieties. Such polymers are readily prepared by the hydrosilylation of 4-vinylcyclohexeneoxide with hydrogen functional polysiloxane in the presence of catalytic amount of platinum or rhodium (299) (eq. 38).

$$\begin{array}{c}
\begin{pmatrix} CH_3 \\ Si-O \\ CH_3 \end{pmatrix}_n \begin{pmatrix} CH_3 \\ Si-O \\ CH_3 \end{pmatrix}_n \begin{pmatrix} CH_3 \\ Si-O \\ CH_3 \end{pmatrix}_n \begin{pmatrix} CH_3 \\ Si-O \\ CH_3 \end{pmatrix}_n$$
(33)

Formation of a siloxane network via hydrosilylation can also be initiated by a free-radical mechanism (300-302). A photochemical route makes use of photosensitizers such as peresters to generate radicals in the system. Unfortunately, the reaction is quite sluggish. Several complexes of platinum such as (\(\Pi_{\text{cyclopentadienyl}}\)) compounds have been found to be photoactive. The mixture of silicone polymer containing alkenyl functional groups with silicon hydride cross-linker materials and a catalytic amount of a cyclopentadienylplatinum(IV) compound is stable in the dark. Under UV radiation, however, the platinum complex undergoes rapid decomposition with release of platinum species that catalyze rapid hydrosilylation and network formation (303-308). Other UV-active hydrosilylation catalyst precursors include (acetylacetonate)Pt(CH₃)₃ (309), (acetylacetonate)₂Pt (310-312), platinum triazene compounds (313, 314), and other sytems (315, 316).

3.13. Characterization of Silicone Networks

The cross-linking of silicones as a function of time can be monitored using a variety of techniques such as infrared spectroscopy, dynamic mechanical analysis, dielectric spectroscopy, ultrasound, differential scanning calorimetry, and thermomechanical analysis (317-324). Infrared spectroscopy is especially useful with addition cure systems because the disappearance of the SiH peak in the starting silicone hydride can be readily monitored. Dynamic mechanical analysis has been used to study the critical time for gelation of a PDMS network (317). Fourier-transform infrared dichroism has been used to investigate the molecular orientation of PDMS networks. In a study of the isothermal dielectric properties of condensation-cured networks at room temperature as a function of catalyst concentration during cure, the effect of catalyst concentration was reflected in the value of the loss factor (318). The gel point of an addition-cured network can be determined using ultrasound techniques (320). A step-like increase in the longitudinal wave velocity is exhibited at the sol–gel transition point. Differential scanning calorimetry has been used with hydrosilylation-cured systems to determine rates of conversion and to develop a kinetic model for the rubber injection-molding process (322).

In addition to the above techniques, inverse gas chromatography, swelling experiments, tensile tests, mechanical analyses, dynamic light scattering, and small-angle neutron scattering have been used to determine the cross-link density of cured networks (325-332). Solid-state ²⁹Si NMR and chemical degradation methods have been used to characterize cured networks structurally (333). ¹H and ²H NMR and spin echo experiments have been used to study the dynamics of cured silicone networks (334-338). Stress relaxation experiments have been employed to examine the chemistry of vulcanized silicone networks (339).

3.14. Model Networks

Construction of model networks allows development of quantitative structure property relationships and provides the ability to test the accuracy of the

Polymerization Page 10 of 11

theories of rubber elasticity (340-343). By definition, model networks have controlled molecular weight between cross-links, controlled cross-link functionality, and controlled molecular weight distribution of cross-linked chains. Silicones cross-linked by either condensation or addition reactions are ideally suited for these studies because all of the above parameters can be controlled. A typical condensation-cured model network consists of an α , α -polydimethylsiloxanediol, tetraethoxysilane (or alkyltrimethoxysilane), and a tin-cure catalyst (344). A typical addition-cure model is composed of α , α -vinylpoly-dimethylsiloxane, M^H_4Q , and a platinum-cure catalyst (345-347).

Using both condensation-cured and addition-cured model systems, it has been shown that the modulus depends on the molecular weight of the polymer and that the modulus at rupture increases with increased junction functionality (348). However, if a bimodal distribution of chain lengths is employed, an anomalously high modulus at high extensions is observed. Finite extensibility of the short chains has been proposed as the origin of this upturn in the stress-strain curve. Calculations have been performed on the effect of including a trimodal distribution of chain lengths on ultimate properties. The study concluded that incorporation of very long chains into a bimodal network of long and short chains could lead to elastomers with improved properties (349). Monte Carlo simulations of the elastic behavior of PDMS networks have been performed (350, 351).

The effect of pendent chains on the mechanical properties of model PDMS has been studied. It was found that the loss modulus of these networks was a function of the concentration and molecular weight of the dangling chains. The elastic properties of networks with pendent chains were found to be lower than those that were completely cross-linked (352).

Monodisperse model networks have been prepared using prepolymers with polydispersivities close to 1.0. Equilibrium tensile measurements on such networks prepared from fractionated PDMS show single-curve elastic moduli of all the networks (353, 354). Simulations of the effect of molecular weight distribution on the equilibrium modulus indicated that with increasing polydispersity, the affine structure factor is found to decrease. Low extents of reaction were observed for the more monodisperse systems. The observed low extent of reaction is due to the reduced number of cross-links with increased molecular weight of chains in the system (355). Dynamic mechanical measurements have been reported for networks prepared by telechelic condensation of monodisperse PDMS with tetraethoxysilane (356). The tensile and swelling behaviors of PDMS networks of high junction functionality have been determined using hydride-terminated and hydride on chain siloxane reactions with vinyl-stopped PDMS (357). In an examination of the mechanical behavior and swelling properties of networks prepared by cross-linking fractionated vinylmethylpolydimethylsiloxane with pentamethylcyclopentasiloxane (358), the dynamic mechanical properties measured were in good agreement with the swelling rates. It has been found that a lowering of the elastic modulus increases broadness of the molecular weight distribution of networks (359). There is a good correlation between theoretical predictions and the experimental value of the tensile modulus for monodisperse networks prepared from vinyl-terminated silicones and MH4Q (333).

3.15. Filled Silicone Networks

Few applications use silicone elastomers in the unfilled state. The addition of fillers results in a severalfold improvement in properties. Fillers can be broadly categorized as reinforcing and nonreinforcing (or semireinforcing). Reinforcing fillers increase tensile strength, tear strength, and abrasion resistance, whereas nonreinforcing fillers are used as additives for reducing cost, improving heat stability, imparting color, and for increasing electrical conductivity (360).

Nonreinforcing fillers include calcium carbonate, clays, silicates, and aluminates. They are primarily used as extending fillers; that is, they serve the purpose of reducing cost per unit volume. Pigment-grade oxides, especially ferric oxides, are used as fillers and stabilizers for high temperature compounds used in oxidizing environments. Other fillers such as fumed titania, alumina, and zirconia find applications for extended heat stability, for imparting color, and for improving the electrical conductivity of the formulation. Although carbon black is the most common reinforcing filler for other vulcanized rubber/elastomeric applications, it is not commonly used as a reinforcing filler in silicones. Instead, it finds applications in improving electrical conductivity and pigmentation (361).

Fillers that are used for providing reinforcement include finely divided silicas prepared by vapor-phase hydrolysis or oxidation of chlorosilanes, dehydrated silica gels, precipitated silicas, diatomaceous silicas, and finely ground high assay natural silicas (362-366). The size, structure, and surface chemistry of the filler all play important roles in determining the final degree of reinforcement (367-369). The most important criteria for reinforcement are the availability of sufficient surface area and a strong van der Waals or hydrogen-bonding interaction between the polymer and the filler (a covalent linkage is not essential) (370, 371). Fillers made by the fumed process have typical surface areas around 200 m²/g and provide the maximum reinforcement. Several comparative studies of the effectiveness of fumed versus precipitated silica show that for fumed silicas, interaction with siloxane occurs by randomly distributed silanols, whereas for precipitated silica, a more complex structure is involved probably involving short chains of polysilicic acid. (365, 372, 373).

Several properties of the filler are important to the compounder (374). Properties that are frequently reported by fumed silica manufacturers include surface area, the acidity of the filler, nitrogen adsorption, oil absorption, and particle size distribution (375, 376). Adsorption techniques provide a measure of the surface area of the filler, whereas oil absorption is an indication of the structure of the filler (377). Measurement of the silanol concentration is critical, and some techniques that are commonly used in the industry to estimate this parameter include methyl red absorption and methanol wettability tests (367, 368, 373). Other techniques to characterize fillers include weight loss, various spectroscopies, such as diffuse reflectance infrared spectroscopy (DRIFT), inverse gas chromatography (IGC), and photoacoustic IR, NMR, Raman, and surface forces apparatus (372, 378-385).

Structuring refers to the formation of an elastic mass before cure that impedes normal processing operations such as molding and extrusion. Intensive working may be required to restore plasticity. Plasticity and process aids are therefore incorporated as monomeric or oligomeric organosilicon compounds. Alternatively, the silanol concentration on the silica surface can be controlled by filler treatment to prevent structuring (386, 387). Reaction of the silica particles with hot vapors of chlorosilanes, low molecular weight cyclic siloxanes, and hexamethyldisilazane (HMDZ) are some of the commonly used filler treatments in the industry (361, 388). It has been proposed that pretreatment of the filler reduces the strength of silica—silica and silica—polymer interactions (389).

Polymer-filler interactions have been studied by deuterium NMR spectroscopy. In unstrained networks, two regions of local chain mobility were identified, that within the absorption layer and that outside. In a uniaxially strained sample, the chains were immobilized near the filler surface. Chain order is increased in filled systems relative to unfilled systems (390). Molecular orientation in stretched networks was also studied using Fourier transform infrared dichroism. Filler introduction led to an increase in orientation, which was attributed to a higher microscopic strain in the elastomeric network (391).

The final mechanical properties of the elastomer compound are a function of the concentration of the reinforcing filler in the formulation. In the small strain limit, Einstein relationships have been proposed for changes in viscosity and modulus as a function of volume fraction of the filler (392, 393). Although these

Polymerization Page 11 of 11

relationships work well for spherical and low structure fillers, they do not correctly predict the final properties of systems filled with high structure nonspherical particles. The high structure of the filler leads to a system that is not free draining, resulting in an augmentation of the filler concentration caused by the rubber trapped in the internal void space (occluded rubber) (394-397). An empirical modification to the Einstein relationship for modulus has been proposed (398). However, these relationships do not account for the secondary agglomeration that results in highly non-Newtonian and thixotropic behavior (399-405). The reasons for improvement in the failure properties of these systems are not well understood (405, 407, 408). Some mechanisms that have been proposed include the ability of a filled system to increase energy dissipation at the tip of the crack through viscoelastic processes, and the ability of the dispersed particles in cooperatively arresting or deflecting the growth of cracks, thereby delaying the onset of catastrophic failure. Results of tensile, IR dichroism, and birefringence experiments show strong upturns in the stress with increasing elongation while segmental—orientation—strain properties remain linear. The upturn in the stress results from limited extensibility of the chains. A model based on Monte Carlo calculations shows strong differences between stress and orientation effects (409). A phenomenon often discussed in connection with filler reinforcement is stress softening, which probably arises because of the progressive detachment, or breaking, of network chains attached to filler particles (410).

Fillers have also been shown to influence abrasive wear of silicone rubbers. The wear rates increase slowly with filler concentration until a critical volume fraction is reached, after which wear rates increase significantly with increasing filler loading. A model, which included the stress concentration induced by the filler, showed a positive correlation between the wear rate and the damage zone volume (411).

A good dispersion of the filler particles is essential for ensuring satisfactory ultimate properties (412-418). The first processing step involves the initial incorporation of the filler in the polymer matrix, and is limited primarily by the wettability of the filler. The next step involves a fracture of the aggregates and their uniform dispersion under shear. Heat treatment is often used to promote wetting and improve polymer–filler interactions (419). Dispersion is measured in terms of the remaining agglomerates, which cause premature failure in tensile testing and other ultimate properties. A trend in obtaining uniform dispersions is *in situ* precipitation of silica by catalytic hydrolysis of tetraethyl orthosilicate (TEOS) in a preformed silicone matrix using sol-gel techniques (420). Dynamic mechanical losses in addition-cured PDMS networks containing *in situ* precipitation of silica indicated that the glass-transition temperature showed only a slight dependence on the presence of the filler particles but the filler reduced both the degree and rate of crystallization for the *in situ* filled networks (421).

< Previous Next >

About Wiley InterScience | About Wiley | Privacy | Terms & Conditions Copyright© 1999-2005 John Wiley & Sons, Inc. All rights reserved.

Silicones

Matthew Butts, GE Global Research Center, Niskayuna, New York
James Cella, GE Global Research Center, Niskayuna, New York
Christina Darkangelo Wood, GE Global Research Center, Niskayuna, New York
Gregory Gillette, GE Global Research Center, Niskayuna, New York
Rachid Kerboua, GE Global Research Center, Niskayuna, New York
John Leman, GE Global Research Center, Niskayuna, New York
Larry Lewis, GE Global Research Center, Niskayuna, New York
Suresh Rajaraman, GE Silicones, Waterford, New York
Slawomir Rubinsztajn, GE Global Research Center, Niskayuna, New York
Florian Schattenmann, GE Global Research Center, Niskayuna, New York
Judith Stein, GE Global Research Center, Niskayuna, New York
Jeffrey Wengrovius, GE Silicones, Waterford, New York
Denyce Wicht, GE Global Research Center, Niskayuna, New York

Encyclopedia of Polymer Science and Technology
Copyright © 2003 by John Wiley & Sons, Inc. All rights reserved.
DOI: 10.1002/0471440264.pst338

Article Online Posting Date: April 15, 2003

< Previous

Bibliography

"Silicones" in *EPST* 1st ed., Vol. 12, pp. 464–569, by H. K. Lictenwalner and M. M. Sprung, General Electric Co.; "Silicones" in *EPSE* 2nd ed., Vol. 15, pp. 204–308, by B. Hardman and A. Torkelson, General Electric Co.

- 1. W. Noll, Chemistry and Technology of Silicones, Academic Press, Inc., New York, 1978.
- 2. E. G. Rochow, Silicon & Silicones, Springer-Verlag, Berlin, 1987.
- 3. D. Hunter, Chem. Week 24 (Feb. 19, 1992).
- 4. A. I. Gorbunfov, A. P. Belyi, and G. G. Filippov, Rus. Chem. Rev. 43, 291 (1974).
- 5. A. D. Petrov, B. F. Mironov, V. A. Ponomarenko, and E. A. Chernyshev, *Synthesis of Organosilicon Monomers*, Consultants Bureau, New York, 1964, p. 36.
- 6. J. M. Zeigler and F. W. G. Fearon, eds., *Silicon-Based Polymer Science* (ACS Advances in Chemistry, Series 224), American Chemical Society, Washington, D.C., 1990.
- 7. F. O. Stark, J. R. Falender, and A. P. Wright, in G. Wilkinson, F. G. A. Stone, and E. W. Abel, eds., *Comprehensive Organometallic Chemistry*, Pergamon Press, Oxford, U.K., 1982, Chapt. "9.3", p. 305.
- 8. C. Eaborn and R. W. Bott, in A. G. MacDiarmid, ed., *The Bond to Carbon*, Vol. I, Part 1, Marcel Dekker, Inc., New York, 1968, p. 105.
- 9. R. J. H. Voorhoeve, Organohalosilanes: Precursors to Silicones, Elsevier, New York, 1967.
- 10. R. R. McGregor, Silicones and Their Uses, McGraw-Hill Book Co., Inc., New York, 1954.
- 11. A. Ladenburg, Ann. Chem. 164, 300 (1872).
- 12. J. J. Ebelman, Compt. Rend. 19, 398 (1844).
- 13. F. S. Kipping, Proc. Chem. Soc. 20, 15 (1904).
- 14. See also W. Dilthey, Chem. Ber. 37, 1139 (1904).
- 15. H. A. Liebhafsky, Silicones under the Monogram, John Wiley and Sons, Inc., New York, 1978.
- 16. A. Stock, *Hydrides of Boron and Silicon*, Cornell University Press, Ithaca, N.Y., 1933, p. 20.
- 17. E. L. Warrick, Forty Years of Firsts, McGraw Hill Book Co., Inc., New York, 1990.
- 18. E. G. Rochow and W. Gilliam, J. Am. Chem. Soc. 63, 798 (1941). Links
- 19. J. F. Hyde and R. DeLong, J. Am. Chem. Soc. 63, 1194 (1941). Links
- 20. V. Chvalovsky, in B. J. Aylett, ed., Organometallic Derivatives of the Main Group Elements, Butterworths, London, 1975.
- 21. T. C. Kendrick, B. Parbhoo, and J. W. White, in S. Patai and Z. Rappoport, eds., The Silicon-Heteroatom Bond,

Bibliography Page 3 of 21

- 52. Ger. Offen. DE 2001303 19710722 (1971), S. Nitzsche, I. Bauer, W. Graf, and N. Zeller; CA 75, 88752.
- 53. H. Watanabe, M. Asami, and Y. Nagai, J. Organomet. Chem. 195, 363 (1980). Links
- 54. U.S. Pat. 4,727,173 (1988), F. D. Mendicino (to Union Carbide); U.S. Pat. 2,473,260 (1949), E. G. Rochow (to General Electric).
- 55. U.S. Pat. 4,778,910 (1988), J. O. Stoffer, J. F. Montle, and N. L. D. Somasivi (to Lopata Research & Development Corp.).
- 56. F. D. Mendicino, H. E. Bartrug, D. J. Boley, P. J. Burns, T. E. Childress, P. J. Collins, N. G. Delong, H. D. Furbee, J. E. Goldsmith, K. W. Hartman, L. G. Hawkins, T. L. Hays, J. W. Heintzman, M. A. Hershman, M. C. Houston, T. G. Hurley, C. S. Knoop, J. P. Kuch, S. Magri, E. E. Malson, W. D. Mercer, S. Miller, L. G. Moody, J. L. McIntyre, S. W. Nichols, R. L. Ocheltree, P. H. Paugh, R. L. Pitrolo, M. R. Powell, T. A. Reed, J. S. Ritschler, C. L. Schilling, J. W. Smith, B. A. Snider, D. M. Wilcox, and J. T. Williams, in H. A. Oeye, ed., Silicon for Chemical Industry IV, Norwegian University of Science and Technology, Trondheim, Norway, 1998, p. 275.
- 57. R. J. Ayen and J. H. Burk, Mater. Res. Soc. Symp. Proc. 73, 801 (1986).
- 58. U.S. Pat. 4,966,986 (1990), R. L. Halm and R. H. Zapp (to Dow Corning).
- 59. U.S. Pat. 4,962,220 (1990), R. L. Halm and R. H. Zapp (to Dow Corning).
- 60. DE 19,817,775 (1999), W. Kalchauer, H. Straussberger, and W. Streckel (to Wacker-Chemie).
- 61. U.S. Pat. 4,965,388 (1990), R. L. Halm, R. H. Zapp, and R. D. Streu (to Dow Corning).
- 62. U.S. Pat. 4,973,725 (1990), K. Lewis (to Union Carbide).
- 63. K. M. Lewis, R. A. Cameron, J. M. Larnerd, and B. Kanner, in Xth International Symposium on Organosilicon Chemistry, Poznan, Poland, 1993, p. 78.
- 64. U.S. Pat. 4,088,669 (1978), J. R. Malek, J. L. Speier, and A. P. Wright (to Dow Corning).
- 65. U.S. Pat. 4,593,114 (1986), K. M. Lewis, B. Kanner (to Union Carbide).
- 66. U.S. Pat. 4,255,348 (1981), B. Kanner and W. B. Herdle (to Union Carbide).
- 67. M. Kumada and K. Tamao, Adv. Organomet. Chem. 6, 19 (1968). Links
- 68. E. Hengge, Topics Curr. Chem. 51, 1 (1974).
- 69. M. Ishikawa, J. Iyoda, H. Ikeda, K. Kotake, T. Hasimoto and M. Kumada, J. Am. Chem. Soc. 103, 4845 (1981). Links
- 70. U.S. Pat. 6,013,824 (2000), L. H. Wood (to Dow Corning).
- 71. R. Calas, J. Dunogues, G. Deleris, and N. Duffaut, J. Organomet. Chem. 225, 117 (1982). Links
- 72. K. Tamao, T. Hayashi, and M. Kumada, J. Organomet. Chem. 114, C9 (1976).
- 73. T. Hayashi, T. Kobayaski, A. Kawamoto, H. Tamashira, and M. Tanaka, Organometallics 9, 280 (1990). Links
- 74. J. D. Rich, J. Am. Chem. Soc. 111, 5886 (1989). Links
- 75. J. D. Rich, Organometallics 8, 2609 (1989). Links
- 76. J. Stein, K. X. Lettko, J. A. King, and R. E. Colborn, J. Appl. Polym. Sci. 51, 815 (1994). Links
- 77. I. Ojima, in S. Patai and Z. Rappoport, eds., *The Chemistry of Organic Silicon Compounds*, John Wiley & Sons, Inc., New York, 1989.
- 78. D. A. Armitage, in Ref. 7, Vol. 2, p. 117.
- 79. J. L. Speier, Adv. Organomet. Chem. 17, 407 (1979). Links
- 80. J. F. Harrod, A. J. Chalk, in I. Wender and P. Pino, eds., Organic Synthesis via Metal Carbonyls, John Wiley & Sons, Inc., New York, 1977, p. 673.
- 81. E. Lukevics, Z. V. Belyakov, M. G. Pomerantseva, and M. G. Voronkov, J. Organomet. Chem. Library 5, 1–179 (1977).
- 82. A. J. Chalk, J. F. Harrod, J. Am. Chem. Soc. 87, 16 (1965). Links
- 83. B. Marciniec, Comprehensive Handbook on Hydrosilylation, Pergamon Press, Oxford U.K., 1992.
- 84. Z. M. Michalska, K. Strzelec, and J. W. Sobczak, J. Mol. Catal., Part A: Chem 156, 91-102 (2000).

- J. Inagaki and Y. Hashimoto, J. Appl. Polym. Sci., Appl. Polym. Symp. 42, 221 (1988).
- D. Huang, R.-Y. Tsai, and F. C. Ho, Proc. SPIE-Int. Soc. Opt. Eng. (Display Devices and Systems) 82, 2892 (1996).
- 207. D. R. Thomas, in S. J. Clarson and J. A. Semlyen, eds., PTR, Prentice Hall, Englewood Cliffs, N.J., 1993.
- 208. "Organic Peroxides," Modern Plastics Encyclopedia, Vol. 62, No. 13, McGraw-Hill, Book Co., Inc., New York, 1993, p. 256.
- 209. U.S. Pat. 2,448,565 (1948), G. Wright and C. S. Oliver (to General Electric).
- 210. M. L. Dunham, D. L. Bailey, and R. M. Miner, Ind. Eng. Chem. 49, 1373 (1957).
- 211. S. W. Kantor, in Abstracts, ACS 130th Meeting, American Chemical Society, Washington, D.C., Sept. 1956.
- 212. U.S. Pat. 2,445,794 (1948), J. Marsden (to General Electric).
- 213. R. J. Cush and H. W. Winnan, in A. Whelan and K. S. Lee, eds., Developments in Rubber Technology, Vol. 2, Applied Science Publishers, Ltd., London, 1981.
- 214. D. Wrobel, in G. Koerner, M. Schulze, and J. Weis, eds., Silicones, Chemistry and Technology, Vulkan-Verlag, Germany, 1991.
- 215. K. E. Polmanteer, Rubber Chem. Technol. 61, 489 (1988).
- 216. J. B. Class and R. P. Grasso, Rubber Chem. Technol. 66, 605 (1993). Links
- 217. J. L. Speier, Adv. Organomet. Chem. 17, 407 (1979). Links
- 218. J. P. Collman and L. S. Hegedus, *Principles and Application of Organotransition Metal Chemistry*, University Science Books, Stanford, Calif., 1980.
- 219. M. A. Brook, Silicon in Organic, Organometallic and Polymer Chemistry, John Wiley & Sons, Inc., New York, 2000.
- 220. U.S. Pat. 5,281,656 (Jan. 25, 1994), L. Thayler, D. Jones, and E. Groenhof (to Dow Corning).
- 221. L. N. Lewis, J. Stein, Y. Gao, R. E. Colborn, and G. Hutchins, Platinum Met. Rev. 41, 66 (1997).
- 222. C. W. Macosko and J. C. Saam, Polym. Bull. 18, 463 (1987). Links
- 223. X. Quan, Polym. Eng. Sci. 29, 1419 (1989). Links
- 224. A. M. Podoba, E. A. Goldovski, and A. A. Dortsov, Int. Polym. Sci. Technol. 14, T/42 (1987).
- 225. A. V. Gorshov, Y. M. Kopylov, A. A. Donstov, and L. Z. Khazen, Int. Polym. Sci. Technol. 13, T/26 (1986).
- 226. A. J. Chalk and J. F. Harrod, J. Am. Chem. Soc. 87, 16 (1965). Links
- 227. L. N. Lewis and N. J. Lewis, J. Am. Chem. Soc. 108, 7228 (1986). Links
- 228. L. N. Lewis, J. Am. Chem. Soc. 112, 5998 (1990). Links
- 229. J. Stein, L. N. Lewis, Y. Gao, and R. A. Scott, J. Am. Chem. Soc. 121, 3693 (1999). Links
- 230. S. Sakaki, N. Mizoe, M. Sugimoto, and Y. Musashi, Coord. Chem. Rev. 190-192, 933 (1999).
- 231. U.S. Pat. 5,331,075 (1994), C. A. Sumpter, L. N. Lewis, and W. B. Lawrence (to General Electric).
- 232. U.S. Pat. 4,603,168 (1986), S. Sasaki and Y. Hamada (to Toray Silicones).
- 233. U.S. Pat. 4,490,488 (1984), R. J. Cush (to Dow Corning).
- 234. U.S. Pat. 3,445,420 (1969), G. J. Kookootsedes and E. P. Plueddemann (to Dow Corning).
- 235. U.S. Pat. 4,336,364 (1982), M. T. Maxson (to Dow Corning).
- 236. U.S. Pat. 4,347,346 (1982), R. P. Eckberg (to General Electric).
- 237. U.S. Pat. 4,256,870 (1981), R. P. Eckberg (to General Electric).
- 238. U.S. Pat. 4,783,552 (1988), P. Y. K. Lo, L. E. Thayer, and A. P. Wright (to Dow Corning).
- 239. U.S. Pat. 4,465,818 (1984), A. Shirahata and S. Shosaku (to Toray Silicones).
- 240. U.S. Pat. 4,472,563 (1987), G. Chandra, P. Y. K. Lo, and Y. A. Peters (to Dow Corning).
- 241. U.S. Pat. 5,122,585 (1992), C. A. Sumpter and L. N. Lewis (to General Electric).
- 242. U.S. Pat. 5,206,329 (1993), C. A. Sumpter, L. N. Lewis, and S. J. Danishefsky (to General Electric).
- 243. P. Steffanut, J. Osborn, and A. DeCian, J. Fisher, Chem. Eur. J. 4, 2008 (1998).

Title Details

Title:	Industrial Minerals and Their Uses - A Handbook and Formulary
Publisher:	William Andrew Publishing/Noyes
Copyright / Pub. Date:	© 1996
ISBN:	0-8155-1408-5
Electronic ISBN:	1-59124-194-4
No. Pages:	632
Author/Editor:	Ciullo, P.A.
Knovel Release Date:	Oct 26, 2001
	This multi-authored handbook is a unique cross-industry resource for formulators and compounders, and an invaluable reference for the producers of formulated commodities and industrial minerals. Monographs on each of the common functional industrial minerals-asbestos, barite, calcium carbonate, diatomite, feldspar, gypsum, hormite, kaolin, mica, nepheline syenite, perlite, pyrophyllite, silica, smectite, talc, vermiculite, wollastonite, and zeolite include an overview of natural and commercial varieties, market size, and application areas. These are supported by descriptions of mineral structures, and the wedding of minerals and chemicals through mineral surface modification.

RUBBER

Peter A. Ciullo
R.T. Vanderbilt Company, Inc.
Norwalk, CT

Norman Hewitt PPG Industries, Inc. Pittsburgh, PA

From Columbus onward, European explorers of Central and South America found the natives exploiting the elastic and water resistant properties of the dried latex from certain trees. The indigenous peoples already knew how to crudely waterproof fabrics and boots by coating them with latex and then drying. They also rolled dried latex into the bouncing balls used for sport. This dried latex became quite a curiosity in Europe, especially among the natural scientists. It received the name "rubber" in 1770 when John Priestly discovered that it could rub out pencil marks.

By the early nineteenth century, rubber was recognized as a flexible, tough, waterproof, and air-impermeable material. Commercial exploitation, however, was stymied by the fact that its toughness and elasticity made it difficult to process. More importantly, articles made from it became stiff and hard in cold weather, and soft and sticky in hot weather. The quest to make useful goods from rubber led Thomas Hancock of Great Britain to invent the rubber band and, in 1820, a machine to facilitate rubber processing. His "masticator" subjected the rubber to intensive shearing that softened it sufficiently to allow mixing and shaping. This development was followed, in 1839, by the discovery of vulcanization, which is generally credited to both Hancock and Charles Goodyear of the United States. Vulcanization – heating an intimate mixture of rubber and sulfur to crosslink the rubber polymer network – greatly improved rubber strength and elasticity and eliminated its deficiencies at temperature extremes. Upon this mechanical and chemical foundation, the rubber industry was born.

The source of rubber latex at that time was the *Hevea brasiliensis* tree, which is native to the Amazon valley. Brazil became the primary source of rubber, but as rubber use grew questions arose as to this country's ability to

Because these compounds are easily colored, they can be made with heat reflective or absorptive colors as required. An alternative approach to weather resistant roofing is to coat a neoprene or EPDM base with CM paint.

The combination of colorability, toughness, environmental durability and resistance to flame, oil, radiation and corrosive chemicals has also secured CSM's widespread use in automotive hoses, tubes, gasketing and wiring, electrical wire insulation for up to 600 volts, wire insulation in nuclear power stations, industrial hoses and tank linings, coated fabrics, hot conveyor belting, and construction coatings and gaskets.

Silicone Rubber

Because of its unique properties and somewhat higher price compared to the other common elastomers, silicone rubber is usually classed as a specialty elastomer, although it is increasingly used as a cost-effective alternative in a variety of applications. Two types of silicone elastomers are available, each providing the same fundamental properties. These are the thermosetting rubbers that are vulcanized with heat, and RTV (room temperature vulcanizing) rubbers.

The basic silicone polymer is dimethylpolysiloxane with a backbone of silicon-oxygen linkages and two methyl groups on each silicon. The silicon-oxygen backbone provides a high degree of inertness to ozone, oxygen, heat (up to 315°C), UV light, moisture, and general weathering effects, while the methyl substituents confer a high degree of flexibility. The basic polymer properties are modified by replacing minor amounts of the methyl substituents with phenyls and/or vinyls. Phenyl groups improve low temperature flexibility (to as low as -100°C) without sacrificing high temperature properties. Vinyl groups improve compression set resistance and facilitate vulcanization. Of the available silicone elastomers – methyl silicone (MQ), methyl-vinyl silicone (VMQ), methyl-phenylsilicone (PMQ), methyl-phenyl-vinyl silicone (PVMQ), and fluoro-vinyl-methyl silicone (FVMQ) – the methyl-vinyl types are most widely used.

Thermal vulcanization typically uses peroxides to crosslink at the vinyl groups of the high molecular weight solid silicone rubbers. Compounded products offer the attributes noted above plus superior resistance to compression set, excellent biocompatability, vibration damping over a wide temperature range, and thermal ablative properties. The latter enables the silicone rubber to form a thermally insulating surface char on exposure to temperatures up to 5,000°C. The rubber remains elastomeric beneath the char. Silicone elastomers generally offer poorer tensile, tear, and abrasion properties than the more common organic rubbers, but this is routinely improved by reinforcement with fumed silica, which also improves electrical insulation properties.

Room temperature vulcanizing (RTV) silicones are low molecular weight dimethylpolysiloxane liquids with reactive end groups. As with the heat cured polymers, there can be minor substitution of methyl groups with phenyls – for improved low temperature flexibility – or with fluoroalkyl groups – for improved oil and solvent resistance and even broader temperature service. Vulcanization of the RTV silicones is obtained from either a condensation or an addition reaction. Condensation cures can be either moisture independent or moisture dependent. For moisture independent compounds, the reactive polymer end group is usually silanol. The crosslinking agent may be a silicone with silanol end groups, using an organic base as the condensation catalyst, an alkoxysilicate (e.g., ethyl silicate), using a metallic salt catalyst, or a polyfunctional aminoxy silicone, often requiring no catalyst. These compounds are known as "two-package" RTVs since the curing agent and/or catalyst is kept separate and added to the compound just prior to use.

Moisture-curing compounds, also known as "one-package" RTVs, are compounded from silanol-terminated polymer with a polyfunctional silane curing agent (e.g., methyltriacetoxysilane) and condensation catalyst, or from a polymer end-stopped with the curing agent. Crosslinking occurs on exposure to atmospheric moisture, starting at the surface and progressing inward with diffusion of moisture into the compound.

Addition-cured RTVs are typically compounded from a dimethylvinylsiloxy-terminated polymer, a polyfunctional silicon hydride crosslinker, and a metal ion catalyst. Vulcanization is independent of moisture and air and forms no volatile byproducts. These products are usually sold as two-package RTVs, but are also available as one-package compounds containing an inhibitor which is volatilized or deactivated by heat to trigger the cure.

Most fabricators of silicone rubber products do not do their own compounding, but purchase premixed compounds requiring only catalyst and/or curing. Solid (thermally cured) rubbers are used in automotive underhood applications, primarily for their heat resistance. Products include ignition cables, coolant and heater hoses, O-rings, and seals. Similar applications are found in aircraft seals, connectors, cushions, and hoses, and in home appliance O-rings, seals, and gaskets. Long service life plus circuit integrity (from ablative charing) and no toxic gas generation have secured the place of silicone rubber in wire and cable insulation for electric power generation and transmission, for naval shipboard cable of all types, and for appliance wiring. The inherent inertness and biocompatibility of silicone rubbers have enabled their use in food contact and medical products. These include baby bottle nipples, belts and hoses for conveying foods and food ingredients, surgical tubing, subdermal implants, and prosthetic devices.

RTV silicones are used by the automotive, appliance, and aerospace industries for electronic potting compounds and formed-in-place gaskets, to form molds for the manufacture of plastic parts, and widely in construction adhesives, sealants, roof coatings, and glazing.

Special Purpose Elastomers

The special purpose rubbers are typically premium priced but cost effective in supplying one or more unique property required for specific demanding applications.

Fluoroelastomers - These are chemically saturated co- and terpolymers of vinylidene fluoride, hexafluoropropylene, tetrafluoroethylene, perfluoro (methyl vinyl) ether, and propylene in various combinations. They are designed to provide extraordinary levels of resistance to oil, chemicals, and heat. They are generally classified into four groups: A, B, F, and Specialty. The lettered groups have increasing fluid resistance, reflecting their increasing flourine levels of 66%, 68%, and 70% respectively. The Specialty group contains further enhanced properties, such as improved low temperature flexibility. Some fluoroelastomers incorporate a brominecontaining curesite monomer and can be vulcanized with peroxides. The rest are most often cured with bisphenol. Because of their exceptional resistance to heat aging and a broad range of chemicals, fuels and solvents, fluoroelastomers are used in a wide variety of demanding automotive, aerospace, and industrial applications. These include seals, gaskets, liners, hoses, protective fabric coatings, diaphragms, roll covers, and cable jacketing.

Polysulfides – The polysulfide rubbers (T) are made by addition of organic halides to a hot aqueous solution of sodium polysulfide. With agitation, the polymer precipitates in the form of small particles which are then washed, coagulated and dried. Linear polysulfides are made by copolymerizing ethylene dichloride and di(chloroethyl) formal with the sulfur linkage. Branched polysulfides are made from di(chloroethyl) formal and 2% trichloropropane. Vulcanized polysulfides are used for their excellent combination of low temperature flexibility, gas and water impermeability, and resistance to ozone, sunlight, heat, weathering, and most oils, solvents and fuels. Linear polymers are cured by zinc oxide, with crosslinking at terminal hydroxy groups. Branched polymers are cured by peroxide (usually zinc peroxide) with crosslinking at terminal thiols. Liquid polysulfide polymers with thiol terminals are also produced. These can be cured at room temperature using peroxides or other oxygen donating curing agents to provide properties similar to the other polysulfide rubbers. The major applications for polysulfides are in products contacting fuels, solvents, or

```
FILE 'HCAPLUS' ENTERED AT 11:23:15 ON 21 JUN 2005
L1
              1 S
                    US20040012159/PN
         211228 S
                     "ADDITION REACTION"+ALL/CT
L2
         184125 S
                     ("ADDITION REACTION"/CT OR "ADDITION
L3
                REACTIONS"/CT OR "EHRLICH REACTION"/CT OR "ADDN. REACTION"/CT
                OR "EHRLICH ADDN. REACTION"/CT OR "FARMER'S RULE"/CT OR
                "MARKOVNIKOV RULE"/CT OR ACETALIZATION/CT OR "ACETALIZATION
                AND KETALIZATION (L) RETRO"/CT OR "ACETALIZATION AND KETALIZATI
                ON (L) STEREOSELECTIVE"/CT OR "ACETALIZATION AND KETALIZATION
                (L) THIO-"/CT OR "ACETALIZATION AND KETALIZATION (L) TRANS-"/CT
                 OR "ACETALIZATION AND KETALIZATION"/CT OR "ADDITION REACTION,
                COORDINATIVE"/CT OR "ADDITION REACTION, COORDINATIVE (L)
                PASSERINI"/CT OR "BARBIER-GRIGNARD REACTION"/CT OR BORATION/CT
                OR BORYLATION/CT OR CHLORAMINATION/CT OR COMPLEXATION/CT OR
                AQUATION/CT OR CHELATION/CT OR "COORDINATION (L) CHELATION,
                TEMPLATE"/CT OR "COORDINATION (L) CHELATION"/CT OR "COORDINATIO
                N (L) INTRAMOL."/CT OR "COORDINATION (L) MOL. RECOGNITION"/CT
                OR "COORDINATION (L) RETRO"/CT OR "COORDINATION (L) STEREOSELEC
                TIVE"/CT OR DEAQUATION/CT OR MASKING/CT OR SEQUESTRATION/CT OR
                COORDINATION/CT OR "COORDINATION THEORY"/CT OR "CYCLOADDITION
                REACTION"/CT OR "ADDITION REACTION (L) RITTER, INTRAMOL."/CT
                OR "ADDITION REACTION (L) AZIRIDINATION"/CT OR "ADDITION
                REACTION (L) ENE, INTRAMOL."/CT OR "DIELS-ALDER REACTION"/CT
                OR "PAUSON-KHAND REACTION"/CT OR "RING CLOSURE AND FORMATION
                (L) ALDER-ENE"/CT OR "RING CLOSURE AND FORMATION (L) KHAND"/CT
                OR "RING CLOSURE AND FORMATION (L) RITTER"/CT OR "RITTER
                REACTION"/CT OR "ENE REACTION"/CT OR "GRIGNARD REACTION"/CT OR
                "GRIGNARD REACTIONS"/CT OR HYDROBORATION/CT OR HYDROCYANATION/C
                T OR HYDROGENATION/CT OR "FISCHER-TROPSCH REACTION"/CT OR
                HYDROHALOGENATION/CT OR HYDRIODINATION/CT OR HYDROBROMINATION/C
                T OR HYDROCHLORINATION/CT OR HYDROFLUORINATION/CT OR HYDROMETAL
                ATION/CT OR HYDROALUMINATION/CT OR HYDROSTANNATION/CT OR
                HYDROSTANNYLATION/CT OR HYDROZIRCONATION/CT OR HYDROSILATION/CT
                 OR HYDROSILYLATION/CT OR "INSERTION REACTION"/CT OR "ARNDT-EIS
                TERT SYNTHESIS"/CT OR "INSERTION REACTIONS"/CT OR KETALIZATION/
                CT OR "MICHAEL CONDENSATION OR MICHAEL REACTION"/CT OR "MICHAEL
                E SILICONE RUBBER/CT
                    "SILICONE RUBBER"/CT OR SILICONE RUBBER OR RTV SILICONE
          25874 S
L4
     FILE 'REGISTRY' ENTERED AT 11:25:53 ON 21 JUN 2005
            708 S (SILICONE OR SILOXANE) AND (VINYL OR ALKENYL)
L5
     FILE 'HCAPLUS' ENTERED AT 11:27:10 ON 21 JUN 2005
          11372 S (L4 AND (?VINYL? OR ALKENYL? OR UNSATURAT?)) OR L5
L6
           4455 S L6 AND (H OR HYDROGEN? OR ORGANOHYDROG? OR ORGANOSILAN?)
L7
           1857 S L7 AND PARTS
L8
L9
            729 s L7 AND WEIGHT
          914 S L7 AND (PER OR PERCENT? OR WT)
2678 S L7 AND COMPOSITION
87514 S ADDITION(2A) (REACT##### OR POLYMERI? OR CURE? OR CURAB?)
342 S ((L2 OR L3) OR L12) AND (L8 OR L9 OR L10 OR L11)
L10
L11
L12
L13
             28 S L13 AND H ATOMS
L14
             19 s L13 AND HYDROGEN ATOMS
L15
            9 S PART (6A) (H OR HYDROGEN?) AND (L14 OR L15)
L16
          25004 S PART (6A) (?ALKEN? OR ?VINYL?)
L17
L18
              6 S L16 AND L17
                SEL PLU=ON L18 1- RN :
     FILE 'REGISTRY' ENTERED AT 11:32:31 ON 21 JUN 2005
L20
             35 s
                    L19
1.21
             14 S
                     L20 AND C/ELS AND SI/ELS
L22
             14 S
                     L21 AND H/ELS
              4 S L22 AND (VINYL? OR ALKEN? OR ETHEN? OR
```

PROPEN? OR ETHYLEN? OR BUTEN? OR PENTEN? OR HEXEN?)

9 ,;

; e r

```
FILE 'HCAPLUS' ENTERED AT 11:34:09 ON 21 JUN 2005
L24
             5 S L18 AND L23
              D ALL HITSTR TOT
            47 S ((L8 OR L9 OR L10 OR L11) OR (L13 OR L14
L25
               OR L15 OR L16) OR L11) AND (H OR HYDROGEN) (3A) DIRECT####
L26
            590 S ((L8 OR L9 OR L10 OR L11) OR (L13 OR L14
               OR L15 OR L16) OR L11) AND (H OR HYDROGEN) (5A) BOND#####
            53 S ((L8 OR L9 OR L10 OR L11) OR (L13 OR L14
L27
               OR L15 OR L16) OR L11) AND (H OR HYDROGEN) (5A) DIRECT#####
            54 S ((L8 OR L9 OR L10 OR L11) OR (L13 OR L14
L28
               OR L15 OR L16) OR L11) AND (SI OR SILICON) (5A) DIRECT#####
            674 S ((L8 OR L9 OR L10 OR L11) OR (L13 OR L14
L29
               OR L15 OR L16) OR L11) AND (SI OR SILICON) (5A) BOND######
            31 S L26 AND L27 AND L28 AND L29
1.30
                   L30 AND (?VINYL? OR ?ETHENY? OR ?ETHENE?
L31
            30 S
               OR ?ETHYLEN?)
L32
            31 S L30 AND L6
     FILE 'STNGUIDE' ENTERED AT 11:38:13 ON 21 JUN 2005
     FILE 'HCAPLUS' ENTERED AT 11:39:21 ON 21 JUN 2005
            31 S (L31 OR L32)
L33
               SEL PLU=ON L33 1- RN: 120 TERMS
L34
    FILE 'REGISTRY' ENTERED AT 11:39:36 ON 21 JUN 2005
           120 s
L36
            51 S
                    L35 AND C/ELS AND SI/ELS
L37
            51 S L36 AND H/ELS
     FILE 'HCAPLUS' ENTERED AT 11:40:11 ON 21 JUN 2005
L38
            26 S L33 AND L37
              D ALL HITSTR TOT
             3 S L30 AND ADDITION####(5A) (REACT######## OR
L39
              POLYMERI? OR VULCAN? OR CROSS########)
       2763585 S L34 3 L39 AND L40
L40
L41
               D ALL HITSTR TOT
```

	CAS/STN FILE	1	'RAPRA' ENTERED AT 12:43:32 ON 21 JUN 2005
L42	1467	S	ADDIT###### (2A) REACT?
L43	170	S	L42 AND (SILICONE? OR POLYSILOX? OR POLYSILICONE? OR SILOXAN?)
L44	86	S	L43 AND RUBBER
L45	21	S	L44 AND (VINYL? OR ETHENYL? OR ALKEN? OR ETHEN?)
L46	13	S	L44 AND (DIVINYL? OR ETHENYL? OR ALKEN? OR ETHEN?)
L47	0	S	L44 AND (TRIVINYL?)
L48	6	S	(L45 OR L46) AND (H OR HYDROGEN)(3A)(DIRECT##### OR SI OR
			SILICON)

	CAS/STN FIL	E 'RAPRA' ENTERED AT 12:43:32 ON 21 JUN 2005
L42	1467	S ADDIT###### (2A) REACT?
L43	170	S L42 AND (SILICONE? OR POLYSILOX? OR POLYSILICONE? OR SILOXAN?)
L44	86	S L43 AND RUBBER
L45	21	S L44 AND (VINYL? OR ETHENYL? OR ALKEN? OR ETHEN?)
L46	13	S L44 AND (DIVINYL? OR ETHENYL? OR ALKEN? OR ETHEN?)
L47	0	S L44 AND (TRIVINYL?)
L48	6	S (L45 OR L46) AND (H OR HYDROGEN)(3A)(DIRECT##### OR SI OR
	ETTE LUCADI	US, RAPRA' ENTERED AT 13:05:12 ON 21 JUN 2005
L49		S HYDROSILYLAT?
L50		S L49 AND (POLYSILICONE OR POLYSILOXAN? OR
T [1		SILOXAN? OR SILICONE)
L51		S L50 AND RUBBER
L52		S L51 AND (H OR HYDROGEN) (4A) (DIRECT##### OR
		SI OR SILICON)
L53	172	
•	•	OR ALKEN? OR ETHEN? OR ALKYLEN?)
L54		S L52 AND (H OR HYDROGEN) (2A) (BOND#### OR
		ATOM)
L55	118	S L53 AND L54
L56	27	S L55 AND (PARTS OR WT OR WEIGHT OR PER OR
		PERCENT?) (3A) (?VINYL? OR DIVINYL? OR TRIVINYL? OR ALKEN? OR
		ETHEN? OR ETHYLEN? OR ALKYLEN?)
L57	6	S L56 AND (MOULD? OR MOLD?)
		D ALL TOT

L24 ANSWER 1 OF 5 HCAPLUS COPYRIGHT ACS on STN

AN 2004:180119 HCAPLUS

DN 140:219230

ED Entered STN: 05 Mar 2004

TI Addition curable-type silicone rubber compositions, blankets, offset printing, thick-film patterns, and plasma display electrodes

IN Takeda, Toshihiko; Shirai, Kenji; Muneta, Akihiro; Meguruya, Noriyuki; Yamakawa, Naoki

PA Dainippon Printing Co., Ltd., Japan; Fujikura Rubber Works Ltd.; Shin-Etsu Chemical Industry Co., Ltd.

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
ΡI	JP 2004067938	A2	20040304	JP 2002-231708	20020808
	JP 2002-231708		20020808		
AB	Title compns. showing	ng hard	ness by duro	meter A (JIS K 6249)	60-95
	after curing compris	se 100 :	parts mixts.	of (A) 20-60	
				and the second of the second	

parts linear organopolysiloxanes having .gtoreq.2 vinyl
groups bonded to Si atoms and showing vinyl group content (x) 1

.times. 10-3-1 .times. 10-5 mol/g and Me content in total org. groups contg. alkenyl groups .gtoreq.90% and (B) 40-80 parts

R3SiO1/2 [R = (un)substituted hydrocarbyl] unit-based copolymers having .gtoreq.2 **vinyl** groups and showing molar ratio R3SiO1/2/SiO2

0.5-1.2 and x 1 .times. 10-2-1 .times. 10-4 mol/g, (C) 2.0-30

parts organohydrogenpolysiloxanes having .gtoreq.2

H atoms bonded to Si atoms and showing SiH group content

0.015-0.0025 mol/g, (D) 0-100 parts inorg. fillers with av.

particle size .ltoreq.50 .mu.m, and (E) 0.5-100 ppm addn. catalysts. The blankets have rubber uppermost layers of the compns. The

patterns and the electrodes are obtained by transferring inks on patterned lithog. plates to the rubber layers of the blankets and then transferring the inks to substrates. Thus, a blanket having a surface rubber layer obtained from a compn. contg. dimethylvinylsilyl

-terminated di-Me polysiloxane, a copolymer comprising Me3SiO1/2, (CH2:CH)Me2SiO1/2, and SiO2, a copolymer comprising Me2HSiO1/2 and SiO2, powd. quartz, and chloroplatinic acid showed high printability.

IT 59942-04-0DP, Dimethylvinylsilyl-terminated dimethyl

siloxane, sru, reaction products with organohydrogenpolysiloxanes

RL: IMF (Industrial manufacture); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)

(rubber; addn. curable-type silicone

rubber compns. for offset printing blankets with high
printability)

RN 59942-04-0 HCAPLUS

CN Poly[oxy(dimethylsilylene)], .alpha.-(ethenyldimethylsilyl)-.omega.[(ethenyldimethylsilyl)oxy]- (9CI) (CA INDEX NAME)

- L48 ANSWER 1 OF 6 RAPRA COPYRIGHT RAPRA on STN
- AN R:926747 RAPRA FS Rapra Abstracts
- TI MOLDABLE SILICONE ELASTOMERS HAVING SELECTIVE PRIMERLESS ADHESION.
- ·IN Ziebell R A
- PA Bryant Rubber Corp.
- PI US 6783858 B2 20040831
- AI US 2001-997473 20011119
- DT Patent
- LA English
- IC ICM B32B0273802738
 - ICS B32B0090400904
- AB Organopolysiloxane compositions, which cure by the addition reaction of silicon-bonded lower alkenyl radicals with silicon-bonded hydrogen atoms and exhibit select adhesion to a variety of substrates, comprise an adhesion promoting mixture consisting of an epoxy-functional compound, soluble polydiorganosiloxanes, polycycloorganosiloxanes (linear and cyclic) and hydroxy end blocked hydrocarbons (glycols), thus giving release characteristics to metal substrates while maintaining adhesion to a thermoplastic substrate. Additionally, an additive may be used to produce surface lubricity after curing.
- CC 45C; 9.12.4T
- SC *ADAUM; ADARE
- CT ADDITION REACTION; ADDITIVE; ADHESION; COMPANIES; COMPANY; COMPOSITION; CURING; CYCLIC; ELASTOMER; EPOXY GROUP; FUNCTIONALITY; LINEAR; LUBRICITY; ORGANOSILICON POLYMER; ORGANOSILICONE POLYMER; ORGANOSILOXANE POLYMER; PLASTIC; POLYORGANOSILOXANE; POLYSILICONE
 - ; POLYSILOXANE; PROPERTIES; RELEASE PROPERTIES; RUBBER
 - ; SILICON POLYMER; SILICON-CONTAINING POLYMER; SILICONE POLYMER
 - ; SILOXANE POLYMER; SOLUBLE; SUBSTRATE; TECHNICAL;
 - THERMOPLASTIC
- NPT GLYCOL; METAL
- SHA ADHESION, silicone rubbers; SILICONE RUBBERS, adhesion
- GT USA

```
L48
       ANSWER 2 OF 6 RAPRA COPYRIGHT RAPRA on STN
      R:909291 RAPRA
                        FS Rapra Abstracts
AN
      MOLDABLE SILICONE ELASTOMERS HAVING SELECTIVE PRIMERLESS
ΤI
      ADHESION.
ΙN
      Ziebell R A
      Bryant Rubber Corp.
PA
      US 6663967 B1 20031216
PΙ
      US 2000-715963 20001117
ΑI
DT
      Patent
LA
      English
            B32B0273802738
IC
      ICM
      ICS
            B32B0090400904
      Disclosed are organopolysiloxane compositions, which cure by the
AB
      addition reaction of silicon-bonded lower
      alkenyl radicals with silicon-bonded hydrogen
      atoms and which exhibit select adhesion to a variety of substrates. The
      compositions comprise an adhesion promoting mixture comprising an
      epoxy-functional compound, soluble polydiorganosiloxanes and
      polycycloorganosiloxanes (linear and cyclic), which give release
      characteristics to metal substrates while maintaining adhesion to the
      thermoplastic substrate. Additionally, an additive may be used to produce
      surface lubricity after curing.
CC
      45C; 9.12.4T
      *KX; UM
SC
      *ADAUM; ADANV
      ADDITION REACTION; ADHESION; ADHESION PROMOTER; COMPANIES;
CT
      COMPANY; COMPOSITION; CURING; CYCLIC; ELASTOMER; FUNCTIONALITY; LINEAR;
      LUBRICITY; ORGANOSILICON POLYMER; ORGANOSILICONE POLYMER; ORGANOSILOXANE
      POLYMER; PLASTIC; POLYORGANOSILOXANE; POLYSILICONE;
      POLYSILOXANE; PRIMERLESS; PROPERTIES; RELEASE PROPERTIES;
      RUBBER; SILICON POLYMER; SILICON-CONTAINING POLYMER;
      SILICONE ELASTOMER; SILICONE POLYMER; SILICONE
      RUBBER; SILOXANE POLYMER; SOLUBILITY; SUBSTRATE;
```

TECHNICAL; THERMOPLASTIC

silicone rubbers

silicone rubbers

SILICONE RUBBERS, adhesion; ADHESION,

SILICONE RUBBERS, adhesion; ADHESION,

NPT

SHR

SHA

GT

METAL

USA

(perfluoropolyether-; curable fluoropolyether-based rubber

52672-74-9, Chloroplatinic acid-1,3-divinyltetramethyldisiloxane

(curable fluoropolyether-based rubber compns. with high

compns. with high hardness and strength)

RL: CAT (Catalyst use); USES (Uses)

hardness and strength)

IT

complex

L24 ANSWER 2 OF 5 HCAPLUS COPYRIGHT ACS on STN

AN 2000:645690 HCAPLUS

DN 133:239058

ED Entered STN: 15 Sep 2000

TI Silicone composition and silicone pressure sensitive adhesive

IN Lutz, Michael Andrew; Watson, Michael John; Mojica, Andrew Anthony

PA Dow Corning Corporation, USA

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
ΡI	EP 1035161	A2	20000913	EP 2000-103762	20000223
	EP 1035161	A 3	20010718		
	EP 1035161	В1	20030423		
	US 6201055	B1	20010313	US 1999-266307	19990311
	NO 2000000880	Α	20000912	NO 2000-880	20000223
	NO 315858	В1	20031103		
	JP 2000265150	A2	20000926	JP 2000-66808	20000310
PRAI	US 1999-266307	Α	19990311		

A silicone compn. for prepg. a silicone pressure sensitive AB adhesive, comprises (A) 20-55 parts polydiorganosiloxane contg. an av. .gtoreq.2 Si-bonded alkenyl groups/mol., (B) 45-80 parts organopolysiloxane resin consisting essentially of R33SiO1/2 units and SiO4/2 units, (C) crosslinker organohydrogenpolysiloxane having an av. .gtoreq.2 Si-bonded H atoms/mol., (D) 25-200 parts SiO2 filler having an av. surface area <25 m2/g, and (E) a hydrosilylation catalyst. Each R3 is independently selected from monovalent hydrocarbon or monovalent halogenated hydrocarbon groups. The mole ratio of R33SiO1/2 units to SiO4/2 units in the (B) organopolysiloxane resin is 0.6-1.5:1 and contains <2 mol% alkenyl groups. The sum of the av. no. of Si-bonded alkenyl groups/mol. in component (A) and the av. no. of Si-bonded H atoms/mol. in component (C) is >4.0. Thus, a compn. contg. 100 parts resin of 70.35 parts MQ resin, 29.15 parts dimethylvinylsilyl-terminated polydimethylsiloxane, 27.2 parts SiO2 (surface area 1.3 m2/q), 1 part crosslinker 1-octadecyl-1,3,5,7,9-pentamethylcyclopentasiloxane, 0.1 part inhibitor, and 0.01 part catalyst formed an adhesive compn. having coeff. of thermal expansion 227 .mu.m/m.degree. and tack 347 g; vs. 266 and 313, resp., without SiO2.

59942-04-0, Dimethylvinylsilyl-terminated polydimethylsiloxane (addn.-curable silicone compn. for pressure-sensitive adhesives with low coeff. of thermal expansion and high tack)

RN 59942-04-0 HCAPLUS

CN Poly[oxy(dimethylsilylene)], .alpha.-(ethenyldimethylsilyl)-.omega.[(ethenyldimethylsilyl)oxy]- (9CI) (CA INDEX NAME)

$$H_2C = CH - Si - O - Si - O - Si - CH = CH_2$$

L24 ANSWER 3 OF 5 HCAPLUS COPYRIGHT ACS on STN

AN 1999:518759 DN 131:177328

TI Addition curable silicone rubber

composition and fluoropolymer-coated electrophotographic fixing
roll using it

IN Yoshida, Takeo; Shudo, Shiqeki; Tomisawa, Nobumasa

PA Shin-Etsu Chemical Industry Co., Ltd., Japan

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
ΡI	JP 11222558	A2	19990817	JP 1998-246569	19980817
	JP 2937198	B2	19990823		
PRAI	JP 1997-350065	A	19971204		

The compn. contains (A) 100 parts organopolysiloxanes contg. .gtoreq.2 alkenyl groups bonded with Si, (B) 0.4-5 M parts [as H based on the alkenyl groups in (A)] organohydrogenpolysiloxane contg. .gtoreq.2 H atoms directly bonded with Si, (C) a catalytic amt. of a Pt (compd.), (D) 5-300 parts cryst. SiO2, and (E) 0.1-20 parts Fe oxide with av. particle size 0.01-0.18 .mu.m. The fixing roll comprises a core rod successively coated with a cured product of the above compn. and a fluoropolymer. The cryst. SiO2 in the rubber compn. was well dispersed for a long time to show high hardness and mech. strength in an improved yield.

(addn. curable silicone rubber

compn. for fluoropolymer-coated electrophotog. fixing roll)

RN 155665-02-4 HCAPLUS

CN Silanediol, dimethyl-, polymer with ethenylmethylsilanediol

IT 59942-04-0 (addn. curable silicone rubber

compn. for fluoropolymer-coated electrophotog. fixing roll)

RN 59942-04-0 HCAPLUS

CN Poly[oxy(dimethylsilylene)], .alpha.-(ethenyldimethylsilyl)-.omega.[(ethenyldimethylsilyl)oxy]-

L38 ANSWER 12 OF 26 HCAPLUS COPYRIGHT ACS on STN

AN 1999:114233 HCAPLUS

130:224222 DN

Adhesive silicone rubber compositions ΤI

Hirai, Nobuo; Ueno, Hideki; Stein, Judith IN

Toshiba Silicone Co., Ltd., Japan PA

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
ΡI	JP 11043608	A2	19990216	JP 1997-200615	19970725
PRAI	JP 1997-200615		19970725		

AB The silicone rubber compns. having excellent

adhesion to thermoplastic resins and poor adhesion to metals, useful for manufq. silicone rubber-thermoplastic resin composites by using molds, comprise (A) polyorganosiloxanes contg. alkenyl

groups, (B) polyorganohydrogensiloxanes having .gtoreq.2 direct

bonding of H with Si, (C) reinforcement

fillers, (D) addn. reaction catalysts selected from Pt

or Pt compds., (E) 1-propoxybenzoate-1,3,5,7-tetramethylcyclotetrasiloxane

(I), and (F) polyorganosiloxanes contg. Ph. Thus, (i) 100 parts dimethylvinyl-terminated polydimethylsiloxane having viscosity

10,000 cP at 25.degree. was kneaded with 40 parts finely powd.

SiO2 (octamethyltetracyclosiloxane-treated Aerosil 200) at 150.degree.,

(ii) mixed with 1.5 parts of a siloxane composed of 67 mol%

MeHSiO1/2 and 33 mol% Me2SiO, 0.3 part Pt-vinylsiloxane complex

soln. (Pt content 0.5 wt.%), and 0.05 part 2-methyl-3-butyn-2-

ol, and (iii) further mixed with 1.4 parts I and 7 parts

of a polyorganosiloxane contq. 28 mol% Ph and having viscosity 200 cP at

25.degree. to give a silicone rubber compn.

The compn. was then injection-molded by using a 2-color

injection molding machine onto a molded-poly(butylene terephthalate) (-----H 01) to make a composite. Their adhesion was excellent while the amt. of the silicone oil bleeding was sufficient to offer easy removal of the composite from the mold.

157578-37-5P ΙT

(rubber; silicone rubber compns. having

excellent adhesion to thermoplastics and poor adhesion to metal molds)

RN 157578-37-5 HCAPLUS

Silanediol, dimethyl-, polymer with .alpha.-(ethenyldimethylsilyl)-.omega.-CN[(ethenyldimethylsilyl)oxy]poly[oxy(dimethylsilylene)] and methylsilanediol (9CI) (CA INDEX NAME)

CM 1

CRN 59942-04-0

CMF (C2 H6 O Si)n C8 H18 O Si2

CCI PMS

```
ANSWER 4 OF 6 HCAPLUS COPYRIGHT 2005 ACS on STN
L57
     1997:761933 HCAPLUS
AN
     128:35871
DN
     Entered STN: 06 Dec 1997
ED
     Liquid silicone rubber compositions with excellent
TI
     pre-cure fluidity and moldability and post-cure fire resistance
     and electric properties
     Matsushita, Takao; Shigehisa, Yasumichi; Tsuji, Yuichi
IN
     Dow Corning Toray Silicone Co., Ltd., Japan
PA
                               DATE
                                          APPLICATION NO.
     PATENT NO.
                        KIND
                                                                 DATE
     -----
                        ____
     EP 808875
PI
                         A1
                               19971126
                                          EP 1997-303555
                                                                 19970523
     EP 808875
                        В1
                               19990915
        R: DE, FR, GB, IT
     JP 09316336
                        A2
                               19971209
                                          JP 1996-152977
                                                                 19960524
                                          US 1997-862113
     US 5973030
                         Α
                               19991026
                                                                 19970522
PRAI JP 1996-152977
                        Α
                               19960524
ΑB
     The title compns. comprise (A) 100 parts polyorganosiloxanes having
     25.degree. viscosity 100-100,000 mPa-s and av. unit formula
     R1aR2bSiO(4-a-b)/2 (R1 = hydrocarbon group excluding alkenyl; R2
     = alkenyl; a = 1.90-2.05; b = 0.0005-0.1; (a + b) =
     1.91-2.06),(B) 10-60 parts fumed silica with sp. surface area .qtoreq.50
     m2/q, (C) 1-200 parts Zn carbonate afforded by treating the surface with
     an organosilicon compd. selected from organosilanes, organosilazanes,
     organosiloxane oligomers, and mixts. thereof, (D) polyorgano
    hydrogen siloxanes comprising .gtoreq.2 Si-
    bonded H in each mol. in a quantity that affords a value
     0.5:1 to 20:1 for the ratio of the no. of moles of Si-
    bonded H to the no. of moles of Si-bonded
    alkenyl in the component A, (E) platinum catalysts in catalytic
     quantity. A compn. comprised 100 parts
    dimethylvinylsilyloxy-endblocked di-Me siloxane, 18
    parts fumed silica, 65 parts Zn carbonate powder, 2 parts
     hexamethyldisilazane, 0.6 part water, 1.4 part trimethylsilyl-terminated
     dimethylsiloxane/methy hydrogen siloxane copolymer, and 10 ppm
     (as Pt) chloroplatinic acid.
    Fire-resistant materials
      Hydrosilylation catalysts
```

ΙT

(liq. silicone rubber compns. with excellent pre-cure fluidity and moldability and post-cure fire resistance and elec. properties)

IT Silicone rubber, properties

RL: POF (Polymer in formulation); PRP (Properties); TEM (Technical or engineered material use); USES (Uses)

(liq. silicone rubber compns. with excellent pre-cure fluidity and moldability and post-cure fire resistance and elec. properties)

L24 ANSWER 4 OF 5 HCAPLUS COPYRIGHT ACS on STN

AN 1998:38500 HCAPLUS

DN 128:106457

TI Dental impression silicone composition

IN Kamohara, Hiroshi; Hattori, Nobuyuki; Komoto, Makiko

PA GC Corporation, Japan; G C Dental Ind Corp.

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
ΡI	DE 19728271	A1	19980108	DE 1997-19728271	19970702
	US 5907002	Α	19990525	US 1997-879190	19970620
PRAI	JP 1996-191643	Α	19960703		

AB A silicone molding material for prepn. of precision dental impressions which polymerizes by an addn. mechanism comprises (a) 100 wt. parts organopolysiloxane contg. .gtoreq.2 aliph. unsatd. hydrocarbon residues; (b) 0.1-30 wt. parts organohydrogen polysiloxane with .gtoreq.3

H atoms bound directly to the Si atom; (c) 10-500 ppm silicone-sol. Pt compd.; (d) 10-500 wt. parts inorg. filler; (e) 5-50 wt. parts fine SiO2 powder with a hydrophobic surface and a BET sp. surface area of 50-500 m2/g; (f) 0.5-50 wt. parts nonionic surfactant; and (g) 10-200 wt

. parts Me Ph polysiloxane. This material has high compression strength, elasticity, and wettability, shows little permanent deformation, and seps. cleanly from the oral tissues without undue discomfort to the patient. Thus, a base paste for dental impressions contained 100 wt. parts di-Me polysiloxane terminated at both ends

with dimethylvinylsilyloxy groups, 3 wt. parts

linear Me H polysiloxane, 10 wt. parts

polyoxyethylene nonylphenyl ether, and 20 wt. parts

quartz. A catalyst paste contained 100 wt. parts

. parts silicone oil contg. 0.4 wt.% 1,3-

divinyltetramethyldisiloxane Pt complex, 10 wt.

parts powd. silica with a hydrophobic surface bearing

trimethylsilyloxy groups, and 20 wt. parts Me Ph

polysiloxane. The 2 pastes were combined in equal amts. and allowed to harden.

IT 2627-95-4D, platinum complexes 59942-04-0

(dental impression silicone compn.)

RN 2627-95-4 HCAPLUS

CN Disiloxane, 1,3-diethenyl-1,1,3,3-tetramethyl- (9CI) (CA INDEX NAME)

RN 59942-04-0 HCAPLUS

CN Poly[oxy(dimethylsilylene)], .alpha.-(ethenyldimethylsilyl)-.omega.[(ethenyldimethylsilyl)oxy]- (9CI) (CA INDEX NAME)

```
ANSWER 5 OF 6 HCAPLUS COPYRIGHT 2005 ACS on STN
L57
     1997:761932 HCAPLUS
ΑN
     128:35870
DN
     Entered STN: 06 Dec 1997
ED
ΤI
     Liquid silicone rubber compositions with excellent
     pre-cure fluidity and moldability and post-cure fire resistance
     and electrical properties
     Matsushita, Takao; Shigehisa, Yasumichi; Tsuji, Yuichi
IN
PA
     Dow Corning Toray Silicone Co., Ltd., Japan
                         KIND
                                                                     DATE
                                DATE
                                             APPLICATION NO.
     PATENT NO.
     -----
                         ____
                                 _____
     EP 808874
                                19971126
                                            EP 1997-303554
                                                                     19970523
PΙ
                          A1
     EP 808874
                         В1
                                19990915
         R: DE, FR, GB, IT
                                             JP 1996-152976
     JP 09316335
                          Α2
                                19971209
                                                                     19960524
                                            US 1997-861542
     US 5880199
                          Α
                                19990309
                                                                     19970522
PRAI JP 1996-152976
                         Α
                                19960524
     The title compns. comprise (A) 100 parts polyorganosiloxanes having
AΒ
     25.degree. viscosity 100-100,000 mPa-s and av. unit formula
     R1aR2bSiO(4-a-b)/2 (R1 = hydrocarbon group excluding alkenyl; R2
     = alkenyl; a = 1.90-2.05; b = 0.0005-0.1; (a + b) =
     1.91-2.06), (B) 10-60 parts silica filler, (C) 1-150 parts Al hydroxide
     powder, (D) 1-150 parts Zn carbonate powder, (E) polyorgano
     hydrogen siloxanes comprising .qtoreq.2 Si-
     bonded H in each mol. in a quantity that affords a value
     0.5:1 to 20:1 for the ratio of the no. of moles of Si-
     bonded H to the no. of moles of Si-bonded
     alkenyl in the component A, (F) 0.001-1 part benzotriazole, (G) Pt
     compd.-3,5-dimethyl-1-hexyn-3-ol reaction mixt. in 1-1000 parts Pt to
     1,000,000 parts the component A, and (H) hydrosilylation catalysts in catalytic quantity. A compn. comprised 100 parts
     dimethylvinylsilyloxy-endblocked di-Me siloxane, 25
     parts fumed silica, 100 parts Al hydroxide powder, 15 parts Zn carbonate
     powder, 1.4 parts dimethylsiloxane/methylhydrogensiloxane copolymer, 0.1
     part benzotriazole, the component G contg. Pt in an amt. of 30 ppm, and 10
     ppm (as Pt) hydrosilylation catalyst.
ΙT
     Fire-resistant materials
       Hydrosilvlation catalysts
        (liq. silicone rubber compns. with excellent
        pre-cure fluidity and moldability and post-cure fire
        resistance and elec. properties)
IT
     Silicone rubber, properties
     RL: POF (Polymer in formulation); PRP (Properties); TEM (Technical or
     engineered material use); USES (Uses)
        (lig. silicone rubber compns. with excellent
        pre-cure fluidity and moldability and post-cure fire
        resistance and elec. properties)
```

L48 ANSWER 3 OF 6 RAPRA COPYRIGHT RAPRA on STN

AN R:659203 RAPRA FS Rapra Abstracts

TI SILICONE GEL COMPOSITIONS.

IN Ikeno M

PA Shin-Etsu Chemical Co.Ltd.

CA Tokyo, Japan

PI US 5599894 A 19970204

AI US 1995-465457 19950605

PRAI JP 1994-148661 19940607

DT Patent

LA English

IC ICM C08G077-08

The above composition comprises (a) 100 pbw of an organopolysiloxane of given average compositional formula, (b) 0.05-10 pbw of an organosiloxane oligomer having alkenyl groups bound to silicon atoms only at the terminal ends of the molecule and at least three such alkenyl groups per molecule, (c) an organohydrogen polysiloxane having at least two hydrogen atoms bound to silicon atoms per molecule, and (d) a catalytic amount of an addition reaction catalyst. The invention also involves electronic materials coated therewith.

CC 45C; 6123

SC *KX; OB

CT APPLICATION; COMPANIES; COMPANY; ELASTOMER; ELECTRONIC APPLICATION; GEL; GELS; PLASTIC; POLYSILOXANE; RUBBER; SILICONE
POLYMER; SILOXANE POLYMER; TECHNICAL; THERMOPLASTIC;
THERMOSET

SHR GELS, siloxane polymers; SILOXANE POLYMERS, gels

GT JAPAN

- ANSWER 6 OF 6 HCAPLUS COPYRIGHT 2005 ACS on STN L57 1996:99477 HCAPLUS AN DN 124:127154 Entered STN: 17 Feb 1996 ED Method for controlling release of an active agent or drug from a TI silicone rubber matrix Bhatt, Padmanabh Pravinchandra; Raul, Victor Albert IN PA Dow Corning Corp., USA DATE APPLICATION NO. PATENT NO. KIND DATE _____ -----EP 688564 A2 19951227 EP 1995-304187 19950616 PΙ EP 688564 A3 19960724 EP 688564 В1 19990804 R: DE, FR, GB, IT JP 08040940 A2 JP 1995-151348 19960213 19950619 US 1995-510249 US 5597584 Α 19970128 19950802 PRAI US 1994-261790 Α 19940620 The disclosed invention is a method for controlling release of active agents or drugs from a silicone rubber matrix by controlling the degree of crosslinking in the matrix. These matrixes are produced from liq. silicone rubbers comprising (A) a polyorganosiloxane contg. at least two alkenyl radicals per mol., (B) an organohydrogensiloxane contg. at least two silicon-bonded hydrogen atoms per mol., and (C) a hydrosilylation catalyst in an amt. sufficient to promote curing of the compn. A liq. silicone rubber was prepd. by combining 10 parts of a mixt. comprising 68% dimethylvinylsiloxy-terminated dimethylsiloxane, a chloroplatinic acid complex of divinyltetramethyldisiloxane dild. with dimethylvinylsiloxy-terminated polydimethylsiloxane with a 1 part of mixt. contg. 87.7% dimethylvinylsiloxy-terminated dimethylsiloxane, 12% trimethylsiloxy-terminated Me H di-Me siloxane, and 0.3% tetramethyltetravinylcyclotetrasiloxane The liq. silicone and oxytetracycline HCl were placed under vacuum and the mixt. was forced into an Al mold at 115.degree.. Drug release from the rod in a buffer soln. and wt. gains due to swelling, were detd. Rubber, silicone, biological studies RL: POF (Polymer in formulation); THU (Therapeutic use); BIOL (Biological study); USES (Uses) (drug release regulation from silicone rubber matrix by controlling degree of crosslinking) Siloxanes and Silicones, biological studies ΙT RL: POF (Polymer in formulation); THU (Therapeutic use); BIOL (Biological
- study); USES (Uses)
 (di-Me, hydroxy-terminated, drug release regulation from
 silicone rubber matrix by controlling degree of
 crosslinking)

```
L48
        ANSWER 5 OF 6 RAPRA COPYRIGHT RAPRA on STN
      R:551293 RAPRA
                         FS Rapra Abstracts
ΑN
      SILICON RUBBER COMPOSITION.
ΤI
      Fuchigami H; Togashi A
TN
      Dow Corning Toray Silicone Co.Ltd.
PΑ
      Mitsui Bldg. No.6, 2-3-16, Nihonbashi-Muromachi, Chuo-Ku, Tokyo 103,
CA
      Japan
      Postcode: 103
      EP 652256 A2 19950510
PΙ
      DE; FR; GB; IT
DS
     EP 1994-117370 19941103
ΑI
PRAI JP 1993-298920 19931104
DT
      Patent
LA
      English
IC
      ICM
           C08L083-07
      ICS
           C08K009-10
AB
      This comprises a diorganopolysiloxane qum, which contains at least 2
      alkenyl groups bonded to silicon atoms in each molecule,
      reinforcing filler, organohydrogenpolysiloxane, which contains at least 2
      hydrogen atoms bonded to silicon atoms in each
     molecule, phenyl group-containing diorganopolysiloxane of which the
      viscosity is 1 to 1000 mm2/S at 25C and an addition
      reaction catalyst, which consists of a platinum catalyst and a
     non-silicone thermoplastic resin having a Tg in the temperature
      range of 50 to 200C and a particle size of 0.01 to 20 micrometers, where
      the amount of the platinum catalyst is 0.01 to 5 wt.% as platinum metal.
      It exhibits excellent storage stability, has a long usable time before
     moulding and good mould release characteristics and makes a
      silicone rubber product with excellent lubricity.
      45C; 6125
CC
SC
      *OD; KX
      ALKENYL GROUP; BLEND; CATALYST; COMPANY; COMPOSITION;
CT
      ELASTOMER; GLASS TRANSITION TEMPERATURE; GUM; LUBRICITY; MOULD RELEASE;
     MOULDABLE; PARTICLE SIZE; PHENYL GROUP; PLASTIC; POLYSILOXANE;
     REINFORCING FILLER; RUBBER; SILICONE ELASTOMER;
      SILICONE POLYMER; SILICONE RUBBER; STORAGE STABILITY;
      TECHNICAL; TG; THERMOPLASTIC; VISCOSITY; MOLD RELEASE; MOLDABLE
NPT ·
      PLATINUM
      SILICONE RUBBERS, blends; BLENDS, silicone
SHR
```

rubbers

JAPAN

GT

L41 ANSWER 2 OF 3 HCAPLUS COPYRIGHT ACS on STN

AN 1995:507866 HCAPLUS

DN 122:242093

ED Entered STN: 26 Apr 1995

TI Silicone rubbers containing tackifiers for good adhesion to organic resins and poor adhesion to metals

IN Fujiki, Hironao; Shudo, Shigeki; Matsuda, Akira

PA Shin-Etsu Chemical Co., Ltd., Japan

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	EP 601883	A2	19940615	EP 1993-309994	19931210
	EP 601883	A3	19951129		
	JP 06172738	A2	19940621	JP 1992-352679	19921210
	JP 3324166	В2	20020917		
	US 5405896	Α	19950411	US 1993-163556	19931209
PRAI	JP 1992-352679	Α	19921210		

AB A tackifier compd. having a silane or siloxane linkage contg. .gtoreq.1 H directly attached to Si and, optionally, a monovalent C1-8 hydrocarbyl group and a linkage contg. an arylene, O, CO, CO2, C(OH), S, or SO2 group and, optionally, an alkyl or alkylene group is used in a silicone rubber compn.

curable by the addn. reaction of vinyl

groups with Si-bonded H. The tackifier

provides good adhesion to org. resins and poor adhesion to metals,

permitting the manuf. of an integral article of the silicone

rubber and an org. resin using a metal mold. Tackifiers

[R(CH2)30-p-C6H4]2CH2 and R(CH2)3OPh (R = 2,4,6,8-

tetramethylcyclotetracyclosiloxan-2-yl) were used in an addn.

reaction-curable siloxane molding compn.

IT 149859-78-9 162456-91-9 162494-51-1 162494-52-2 162494-53-3 162494-54-4 (tackifiers; in curable **silicone rubbers** for adhesion to plastics but not to metal molds)

RN 149859-78-9 HCAPLUS

CN Cyclotetrasiloxane, 2,4,6,8-tetramethyl-2-(3-phenoxypropyl)-

RN 162456-91-9 HCAPLUS

CN Cyclotetrasiloxane, 2,2'-[methylenebis(4,1-phenyleneoxy-3,1-propanediyl)]bis[2,4,6,8-tetramethyl-(9CI) (CA INDEX NAME)

ANSWER 6 OF 6 RAPRA COPYRIGHT RAPRA on STN L48 R:504478 RAPRA FS Rapra Abstracts AN SILICONE COMPOSITE PRODUCT AND PROCESS FOR PREPARING THE SAME. Ikeno M; Fujiki H IN Shin-Etsu Chemical Co.Ltd. PA CA Tokyo, Japan PΙ US 5279890 A 19940118 US 1990-623681 19901206 ΑI PRAI JP 1989-318627 19891207 Patent DTEnglish LA ICM B29C039-12 IC ICS B32B007-02 The composite product comprises a silicone gel, obtained by AB curing an addition curable organopolysiloxane composition, and an elastomer layer or resin layer integrally formed on the gel by the use of an organopolysiloxane having Si-bonded alkenyl groups and Si-bonded hydrogen atoms. CC 45C; 626 SC *OK; KX ADDITION REACTION; COMPANY; COMPOSITE; CURING; ELASTOMER; GEL; CTMANUFACTURE; ORGANOSILOXANE POLYMER; POLYORGANOSILOXANE; POLYSILOXANE; RUBBER; SILICONE POLYMER; TECHNICAL; THERMOSET COMPOSITES, siloxane polymers; SILOXANE SHR

POLYMERS, composites

JAPAN

GT

- L41 ANSWER 3 OF 3 HCAPLUS COPYRIGHT ACS on STN
- AN 1992:184547 HCAPLUS
- DN 116:184547
- ED Entered STN: 03 May 1992
- TI Heat-fixing roller for electrophotography
- IN Kon, Shuji; Iwata, Toshimitsu; Kanekura, Yoshiaki; Oya, Masaaki; Menjo, Takeshi; Sakurai, Masaaki
- PA Canon K. K., Japan; Shava Electric Wire and Cable Co., Ltd.

(FILE 'HOME' ENTERED AT 11:22:52 ON 21 JUN 2005)

PATENT NO.	KIND	KIND DATE APPLICATION NO.	DATE	
PI JP 03033786 PRAI JP 1989-168957	A2	19910214 19890629	JP 1989-168957	19890629

The title heat-fixing roller has on a metal mandrel (a) an elastic layer AB of silicone rubber, (b) an oil barrier layer of fluororubber, and (c) a mold-releasing layer having a compn. contg. 100 wt. part methylvinylpolysiloxane (degree of polymn. 5,000-12,000) having .gtoreq.2 vinyl groups per 1 mol., 1-100 wt. part methylvinylpolysiloxane having .gtoreg.1 SiCH:CH2 and 0.5-1.5:1 (R1) 3SiO1/2 or (R1) 2R2SiO1/2 (R1, R2 = Me, vinyl) and SiO4/2 units, a crosslinking agent methylhydrodienepolysiloxane having .gtoreq.2 H directly bonded to the Si atom amounting to give SiH/SiCH: CH2 of the entire polysiloxane in the mold-releasing layer mol. ratio of 0.5-20, and an addn. reaction catalyst Pt compd. The mold-releasing layer preferably contains .ltoreq.30 wt. part methylvinylsilicone rubber blocked with vinyl groups on both termini having viscosity 5,000-30,000 cst. This heat-fixing roller which uses an oil as a mold-releasing agent to prevent offset to the roller is used in the heat-fixation part of an electrophotog. machine or statog. copier and provides excellent size-stability, high reliability, high quality images, and excellent durability.

L38 ANSWER 23 OF 26 HCAPLUS COPYRIGHT ACS on STN

AN 1992:22684 HCAPLUS

DN 116:22684

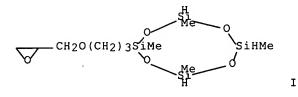
ED Entered STN: 24 Jan 1992

TI Addition-curable organopolysiloxane adhesive compositions

IN Okami, Takehide

PA Shin-Etsu Chemical Industry Co., Ltd., Japan

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
ΡI	JP 03163183	A2	19910715	JP 1989-303571	19891122
	JP 07039571	B4	19950501		
	US 5312855	Α	19940517	US 1993-11832	19930201
PRAI	JP 1989-303571	A	19891122		
	US 1990-616568	В1	19901121		



The title compns. contain 100 parts .gtoreq.2 AΒ alkenyl-contg. organopolysiloxanes with viscosity (25.degree.) 100-200,000 cSt, organohydrogenpolysiloxanes contg. .gtoreq.2 H directly bonded to Si which may supply 0.6-6.0 (based on 1 alkenyl group) H, catalytic amt. of Pt or Pt compds., 0.5-20 parts Si compd. tackifiers contq. .qtoreq.1 H directly bonded to Si, and 0.05-5 parts .gtoreq.2 allyl ester group-contg. compds. Thus, 100 parts dimethylvinylsiloxy -terminated dimethylpolysiloxane (viscosity 5000 cSt) was mixed with trimethylsilyl-treated fumed silica (sp. surface area 300 m2/g) 15, 2% Pt+contg. H2PtCl6 octanol soln. 0.02, 3-methyl-3-hydroxy-1-butyne 0.005, Me2SiHO(SiMeHO)3(SiMe2O)10SiHMe2 2.5, tackifier I 3.0, and triallyl trimellitate 0.8 part to give an adhesive compn., which was cured at 120.degree. for 60 min to give a product showing JIS A hardness 35, elongation 320%, and tensile strength 31 kg/cm2. Then, the compn. was sandwiched with various adherents, e.g. glass, metals, polyesters, epoxy resins, then pressed and cured to give test pieces with shear strength 10-12 kg/cm2 initially and 10-11 after 3 days in water at 80.degree..

IT 138220-10-7

(tackifiers, silicone rubber adhesive
compns. contq.)

RN 138220-10-7 HCAPLUS

CN 1,2,4-Benzenetricarboxylic acid, 1-[3-(pentamethyldisiloxanyl)propyl] 2,4-di-2-propenyl ester (9CI) (CA INDEX NAME)